

**FINAL REPORT—ARSENIC
STABILIZATION RESEARCH PROJECT**

**MINE WASTE TECHNOLOGY PROGRAM
ACTIVITY IV, PROJECT 5**

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Final Report—Arsenic Stabilization Research Project

Mine Waste Technology Program Activity IV, Project 5

Demonstration performed by:

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Disclaimer

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Foreword

Today, industries are developing and modifying technologies to more efficiently produce their products. The waste generated by these industries, if improperly dealt with, can threaten public health and degrade the environment. The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's land, air, and water resources; and under mandate of national environmental laws, the EPA strives to formulate and implement actions leading to a balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define, measure the impacts, and search for solutions for environmental problems.

The National Risk Management Research Laboratory (NRMRL) of EPA is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. The Federal Energy Technology Center (FETC) of the Department of Energy (DOE) has responsibilities similar to NRMRL in that FETC is one of several DOE centers responsible for planning, implementing, and managing research and development programs. In June 1991, an Interagency Agreement was signed between EPA and DOE that made funds available to support the Western Environmental Technology Office's operating contractor, MSE Technology Applications, Inc., and Montana Tech of The University of Montana for developing the Mine Waste Technology Program (MWTP). This publication is one of the products of the research conducted by the MWTP through these two Federal organizations and provides a vital communications link between the researcher and the user community.

The objectives of Activity IV, Project 5, were to develop a technique for removing arsenic from wastewaters to below the U.S. Drinking Water Standard, i.e., 50 parts per billion, and to demonstrate that the arsenic bearing solids produced were stable for long-term storage in outdoor chemical ponds. This process evaluated the effectiveness of removing arsenic from synthetic laboratory solutions and from two industrial waters, i.e., an acid mine water (Berkeley Pit water) and an industrial wastewater (ASARCO scrubber blow down water). The solids produced from the water treatment were exposed to air for an extended period of time to demonstrate stability in a chemical pond environment.

Executive Summary

Arsenic removal from wastewaters has been successfully practiced for many years, i.e., technologies have been available to lower the arsenic concentration of wastewaters to below the U.S. Drinking Water Standards (< 50 parts per billion). However, one of the major technologies, i.e., lime neutralization, produces sludges that cannot be safely stored in outdoor tailings ponds. These sludges release the arsenic back into the solution phase as the calcium arsenate compounds convert to calcium carbonate (caused by carbon dioxide in air). The other major industrial technology, i.e., ferrihydrite precipitation with concurrent adsorption of arsenic onto the ferrihydrite surface, produces sludges that may not be stable under long-term storage conditions because the amorphous ferrihydrite is not a thermodynamically stable phase. The thermodynamically stable phase is hematite or goethite, so eventually the meta-stable ferrihydrite will convert to a more stable equilibrium phase. When this conversion occurs, the surface area of the initial ferrihydrite will be greatly decreased; and when the surface area decrease occurs, arsenic is likely to be desorbed from the solid surface back into the solution phase.

The present study has solved the stability problem suffered by the above mentioned technologies, i.e., compounds are formed that are stable against conversion to calcium carbonate, and since the arsenic sequestration is via compound formation (rather than an adsorption phenomena), the solids are not dependent upon maintaining a certain surface area.

This study has demonstrated that apatite-like compounds, $\text{Ca}_{10}(\text{As}_x\text{P}_y\text{O}_4)_6(\text{OH})_2$, are formed via a simple precipitation process, i.e., phosphate is added to the arsenic bearing solution in prescribed amounts to facilitate the formation of arsenatephosphateapatite compounds. These compounds have an exceedingly low solubility under tailings pond pH conditions, and they are more stable than calcium carbonate so that long-term safe storage is ensured.

Recipe

A *recipe* for effective arsenic removal from solution and subsequent stability in tailings pond environments was formulated. The *recipe* requirements are presented below.

- C Arsenic must be in the arsenate rather than arsenite form.
- C Phosphate is required for a stable, storable, solid product to be formed. The phosphorus/arsenic (P/As) mole ratio in the initial solution phase must be equal to or greater than 5.
- C The Ca/(As+ P) mole ratio in the initial solution phase must be greater than 1.5 times the stoichiometric requirement for formation of the apatite-like compound and for the formation of calcium sulfate (if the water contains sulfate).

Project Results

The positive project results are presented below.

- C Arsenate was stripped from aqueous solutions but phosphate enhanced the effectiveness of the precipitation, i.e., the effectiveness was enhanced by controlling the P/As mole ratio in the initial solution phase (see Table ES-1).

Table ES-1. Effectiveness of arsenic removal by phosphate.

System (initial arsenate concentration)	Arsenic after treatment, Fg/L		
	P/As = 0	P/As = 5	P/As = 7
Pure Synthetic Water (initial As was 1,000,000 Fg/L)	58	< IDL	-
Berkeley Pit Water (initial As was 100,000 Fg/L)	14	14	< IDL
ASARCO Water (initial As was > 3,000,000 Fg/L)	2776	19	24
The Ca/(As+P) mole ratio for the pure system was 3.7. The Ca/(As+P) mole ratios for the Berkeley Pit and ASARCO systems were 2.5. P/As = mole ratio in the initial solution prior to precipitation. Instrument Detection Limit = 1.4 Fg/L			

- C A series of arsenate bearing hydroxyapatite solid solutions were formed by controlling the P/As mole ratio in the initial solution prior to precipitation (see Table ES-2). Laboratory studies showed that solid solutions containing arsenic concentrations from a few percent to approximately 30% readily formed. These are new compounds that were not reported previously. The new compounds stoichiometry were identified by chemical digestions and their structures by X-ray diffraction and X-ray photoelectron spectrometry.

Table ES-2. Hydroxyapatite solid solution series.

P/As mole ratio in the final solid	$\text{Ca}_w(\text{As}_x\text{P}_y\text{O}_6)_z(\text{OH})_2$				Arsenic in the final solid, %
	w	x	y	z	
0.06 ± 0.01	10	0.94	0.06	6	28.6 ± 0.7
0.6 ± 0.1	10	0.63	0.37	6	18.5 ± 2.1
1.9 ± 0.0	10	0.35	0.66	6	13.7 ± 0.4
5.7 ± 0.4	10	0.15	0.85	6	5.9 ± 0.3
8.0 ± 0.2	10	0.11	0.89	6	4.4 ± 0.2
7.9 ± 0.1	10	0.11	0.89	6	4.3 ± 0.2
12.7 ± 0.2	10	0.01	0.99	6	2.9 ± 0.1
No As	10	0.00	1.00	6	0.1 ± 0.02
Apatite	10	0.00	1.00	6	0

- C The free energies of formation for the APHAP compounds were determined (see Table ES-3), which allows modeling of the stability of the compounds under various solution conditions. One of the important considerations was whether the compounds would be stable to long-term storage in

tailings pond environments, i.e., exposure to air. Previously, Dr. R. G. Robins (1985) demonstrated that calcium arsenate compounds were unstable in air because the carbon dioxide in air reacts with the calcium arsenate to form calcium carbonate (with the release of arsenic back to the solution phase). Modeling (using the free energy of formation data collected in this study) of tailings pond conditions showed that compound stability is a function of P/As mole ratio, e.g., compounds with a P/As mole ratio greater than five should be stable to air exposure in tailings-pond-type storage conditions.

Table ES-3. Solid solution stoichiometry versus free energy of formation.

Compound Stoichiometry) G°, Free energy of formation	
	kcal/g-mole	kJ/g-mole
$\text{Ca}_{10}(\text{As}_{0.94}\text{P}_{0.06}\text{O}_4)_6(\text{OH})_2$	-2,466.1 ± 3.7	-10318.2 ± 15.5
$\text{Ca}_{10}(\text{As}_{0.63}\text{P}_{0.37}\text{O}_4)_6(\text{OH})_2$ (non-QA)	-2671.0 ± 16.0	-11175.4 ± 66.9
$\text{Ca}_{10}(\text{As}_{0.34}\text{P}_{0.66}\text{O}_4)_6(\text{OH})_2$ (non-QA)	-2826.9 ± 1.6	-11827.7 ± 6.7
$\text{Ca}_{10}(\text{As}_{0.15}\text{P}_{0.85}\text{O}_4)_6(\text{OH})_2$	-2932.4 ± 9.3	-12269.2 ± 38.9
$\text{Ca}_{10}(\text{As}_{0.11}\text{P}_{0.89}\text{O}_4)_6(\text{OH})_2$	-2952.4 ± 4.7	-12352.8 ± 19.7
$\text{Ca}_{10}(\text{As}_{0.07}\text{P}_{0.93}\text{O}_4)_6(\text{OH})_2$	-2973.2 ± 4.2	-12439.9 ± 17.6
$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	-3014.0 ± 4.2	-12610.6 ± 17.6
$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, Literature value	-3014.3	-12611.8

- C The long-term stability of the apatite-like compounds is presently being assessed, i.e., compound stability is being tested by sparging air into aqueous/compound slurries for extended periods of time (data for 6-month stability has been collected; the test monitoring will continue for another 1½ years). The pH, E_H , and solution arsenic, phosphorus, and calcium concentrations are being monitored as a function of aging time. The 6-month data showed that the arsenic (no phosphate present) bearing solids slurries are not stable to air exposure (see Table ES-4). The arsenic/phosphorus bearing solids were all stable to 6-month air exposure, i.e., all samples for all waters under testing (pure system, Berkeley Pit system, and the ASARCO system) showed an arsenic solubility of less than 50 parts per billion.

Table ES-4. Arsenic in solution after aging for 6 months.

System (initial arsenic concentration)	Arsenic in solution after aging for 6 months, Fg/L
Pure (initial As was 1,000,000 Fg/L)	3.4 ± 1.0
Berkeley Pit Water (initial As was 100,000 Fg/L)	7.5 ± 2.4
ASARCO Water (initial As was > 3,000,000 Fg/L)	28.9 ± 0.6
Nominal P/As mole ratio in the starting solution = 7. Precipitation was conducted at ambient temperature. Six-month aging in air-sparged vessels.	

A first order economic analysis suggested that the cost of applying the apatite-like precipitation process to low arsenic bearing minewaters is reasonable, e.g., the cost was estimated to be approximately 74 ± 21 cents/1000 gallons. The estimated cost for treating a very high arsenic bearing wastewater like

the ASARCO blowdown water was considerably higher, e.g., the cost was estimated to be approximately 1.8 ± 0.5 cents/gallon. These costs were competitive with other lime neutralization processes.

Future Demonstrations

The Mine Waste Technology Program at MSE Technology Applications, Inc., will be evaluating the apatite-like process during the summer of 1997 at two separate sites, i.e., an acid mine drainage site in Montana (to be selected) and the ASARCO smelter site in East Helena, Montana. The evaluation will be conducted on a high arsenic (1–3 grams per liter), low flow rate system (the smelter site) and a low arsenic (400–500 parts per billion), high flow rate system (acid mine drainage site).

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Abbreviations, Acronyms, and Symbols

AHAP	arsenatehydroxyapatite, $\text{Ca}_{10}(\text{AsO}_4)_6(\text{OH})_2$
APHAP	arsenatephosphatehydroxyapatite, $\text{Ca}_{10}(\text{As}_x\text{P}_y\text{O}_4)_6(\text{OH})_2$
As	arsenic
BPIT	Berkeley Pit
Ca	calcium
cc	cubic centimeter
CCV	continuing calibration verification
CRDL	contract required detection limit
DOE	U.S. Department of Energy
E_H	oxidation-reduction potential
EPA	U.S. Environmental Protection Agency
FAP	ferricarsenatephosphate, $\text{Fe}(\text{As}_x\text{P}_y)\text{O}_4$
FCAC	factored capital annual cost
FCC	factored capital cost
g	gram
g/L	gram per liter
HAP	hydroxyapatite
HDPE	high density polyethylene
IAG	interagency agreement
ICP	Inductively Coupled Plasma
ICV	initial calibration verification
IDL	instrument detection limit
kcal/g-mole	kilocalories per gram-mole
kJ/g-mole	kilojoule per gram-mole
LCS	laboratory control sample
M&S	Marshall and Swift
mg/L	milligram per liter
MWTP	Mine Waste Technology Program
P	phosphorus
ppb	parts per billion
ppm	parts per million
QA	Quality Assurance
QA/QC	Quality Assurance/Quality Control
QAPP	Quality Assurance Project Plan
RCRA	Resource Conservation and Recovery Act
RPD	relative percent differences
SEM-EDX	Scanning Electron Microscopy with Energy Dispersive Analysis Capabilities
TCLP	Toxicity Characteristic Leaching Procedure
XPS	X-ray photoelectron spectrometry
XRD	X-ray diffraction
µg/L	micrograms per liter
ΔG	free energy
ΔG°	standard free energy

(activity coefficient

1. Introduction

This final report presents the information and results compiled by Montana Tech of the University of Montana for the Mine Waste Technology Program (MWTP), Activity IV, Project 5—Removal of Arsenic from Waste Solutions as Storable Stable Precipitates. The research described in this report was conducted in accordance with the requirements of the Interagency Agreement (IAG), Activity IV, Scope of Work. The IAG was signed in June 1991 by the U.S. Environmental Protection Agency (EPA) and the Department of Energy (DOE) to initiate work on the MWTP. The work plan for MWTP Activity IV, Project 5, addresses testing and evaluating technology applicable to remediation of the EPA Technical Issue: Mobile Toxic Constituents—Water. The analytical methods and bench-scale treatment testing conducted for this study were consistent with EPA's requirements outlined in the project-specific Quality Assurance Project Plan (QAPP) for the Removal of Arsenic from Waste Solutions as Storable Stable Precipitates (Ref. 1). This final report describes the work that was conducted and summarizes the technical results that were obtained to evaluate treatment technologies for acid mine waters. Refer to the QAPP for the detailed descriptions of the process operations.

1.1 Background

1.1.1 Arsenic Species Removal from Waste Solutions

Robins (Refs. 2–5) demonstrated in the 1980s that lime precipitation of calcium arsenate with subsequent storage in a tailings pond environment is unacceptable because at pH levels above approximately 8.2 calcium arsenate will be converted to calcium carbonate (by carbon dioxide in air) resulting in the release of arsenic

into the aqueous phase. Arsenic removal by precipitation as calcium arsenate was discontinued by industry and replaced by arsenic adsorption on a ferric hydroxide precipitate (called the ferrihydrite process). Ferrihydrite precipitation was selected as EPA's Best Demonstrated Available Technology for removing arsenic from wastewater solutions (Ref. 6). However, even though low concentrations of arsenic in solutions can be achieved by ferrihydrite precipitation, Robins and Khoe, et al. (Refs. 7,8) and Waychunas, et al. (Ref. 9) demonstrated that the removal from solution is actually an adsorption phenomena. Schwertmann, et al. (Refs. 10, 11) demonstrated that ferrihydrite (an amorphous ferric oxyhydroxide solid) converts to its more thermodynamically stable crystalline form (goethite or hematite) with aging time. This conversion results in a decrease in surface area with the potential release of adsorbed species back into the solution phase. Therefore, long-term stability of such residues in tailings pond environments may not be appropriate.

1.1.2 Stability of Mineral-Like Residues

The approach taken during this study was to form a mineral-like phase that showed equilibrium phase stability under tailings pond environmental conditions. If equilibrium phase stability is achieved (for a given environment) then long-term stability would be ensured (at least for as long as the environmental conditions are maintained). The study investigated the formation of arsenic precipitates in two systems, i.e., the calcium-arsenate-phosphate (apatite-like solid solutions of arsenate and phosphate) system, and the ferric-arsenate-phosphate water (compounds containing iron, arsenate and phosphate) system. Both of these systems show great promise for industrial application.

2. Objectives of Present Study

The objectives of the present study are listed below.

- C **Collecting data** to optimize the conditions necessary for maximum removal of arsenic from waste solutions and the formation of arsenic bearing precipitates. The goal was to lower the arsenic concentration to below 50 micrograms per liter ($\mu\text{g/L}$).
- C **Characterizing** the chemical and structural properties of the precipitated **mineral-like phases**.
- C **Demonstrating the chemical stability** of the precipitated phases to tailings pond environmental conditions, i.e., exposure to air at tailings pond pH levels.
- C **Developing** a first order **economic evaluation** for the proposed treatment process.

3. Technical Program

3.1 Background

The objectives of this project were to strip arsenic from solutions in a manner to produce mineral-like precipitated products that are stable for long-term storage in tailings-pond-type environments. It was proposed by the principal investigator of this project that this may be accomplished by precipitation performed from solutions containing arsenate and phosphate.

It was postulated that calcium arsenatehydroxyapatite, $\text{Ca}_{10}(\text{AsO}_4)_6(\text{OH})_2$, AHAP, or calcium arsenatephosphate-hydroxyapatite, $\text{Ca}_{10}(\text{As}_x\text{P}_y\text{O}_4)_6(\text{OH})_2$, APHAP, could be formed at ambient temperature. This postulate was based on previous work conducted by Twidwell, Dahnke, and Plessas (reported in the original proposal and described in the following sections).

3.1.1 Previous Studies

The problem of safely disposing of arsenic bearing aqueous solutions is significant and has yet to be solved. Efforts at Montana Tech are directed toward studies that may produce an acceptable solution to the arsenic solution disposal problem, i.e., the formation of stable arsenic bearing phases stable for long-term outdoor storage. There have been a number of arsenic removal/stabilization studies at Montana Tech (under the direction of L. G. Twidwell) that have led up to the present study. Previous work was summarized by Twidwell (Ref. 12), and his summary is presented below to illustrate the progression of thesis work leading to the present study.

Studies at Montana College of Mineral Science and Technology, Arsenic Removal From Solution

Twidwell (Refs. 13, 14), Comba (Refs. 15, 16), and Plessas (Ref. 17) have investigated the

removal of arsenic from process and wastewater solutions by formation of filterable precipitates. The philosophy of the research was to form mineral-like precipitated solids that are stable in normal storage environments.

Comba (Ref. 15) investigated the removal of arsenic from solution by the formation of mimetite, a lead chloroarsenate $[\text{Pb}_5(\text{AsO}_4)_3\text{Cl}]$. His results demonstrated techniques for successfully stripping aqueous arsenic concentrations from several grams per liter to below ICP detection limits for arsenic, i.e., the arsenic concentration was lowered to below 0.2 micrograms/liter (ppb), and also demonstrated the formation of phosphate/arsenate solid solution solids (phosphomimetite). The free energy of formation for mimetite was determined to be -625 ± 2 kilocalories/mole. The filterability of the mimetite was excellent because the morphology of the precipitate was small crystalline spherites. The lead left in solution could be stripped from solution as lead phosphate by the addition of phosphoric acid or by cationic ion exchange.

Because the lead chloroarsenate test work was successful, attempts to form other chloro-, hydroxy- and phospho-arsenates (apatite like precipitates) have been made. Dahnke (Ref. 18) initiated a series of tests to investigate the formation and stability of phosphate/arsenate compounds. His experimental test work consisted of bottle equilibrations. He set up multiple bottles into which he placed solutions of arsenic, arsenic plus phosphorus, and arsenic plus chloride. To each bottle solution he added a different amount of lime (there were twenty bottles in each series). Each solution was sampled as a function of time and was analyzed by ICP for arsenic. The results of this test work showed that the presence of phosphorus (in the initial solutions) was necessary to ensure low

concentrations of arsenic in the aged solutions, i.e., without phosphorus the measured arsenic concentrations were in the tens to hundreds of parts per million (ppm) range but with phosphorus initially present the aged solutions contained < 1 ppm (the instrumentation available at that time had a detection limit for arsenic of about 1 ppm). At the end of Dahnke's tenure at Montana Tech, the samples were stored in closed polyethylene bottles.

Approximately four years later Plessas reanalyzed a portion of the solutions (Ref. 17). The samples containing phosphate showed an arsenic concentration of only a few parts per billion (ppb). A few of Plessas's analyses are presented in Table 3.1 (Plessas, Ref. 17; Twidwell, et al., Ref. 14).

The excellent stability results reported by Plessas for the phosphate/arsenate bearing solids (at pH levels present in tailings ponds) were the basis for initiating the present study. The present study was performed by four graduate students, i.e., Paul Miranda (Ref. 19), Travis Orser (Ref. 20), Jennifer Saran (Ref. 21) and Shannon Wilson (Ref. 22).

Other Studies

There are only a few other references relevant to the present study, e.g., Nikolaev, Masurova, Serdjuk, and Shemonaeva (Refs. 23, 24), Liao (Ref. 25), Mahapatra, Mahapatra, and Mishra (Ref. 26) and Gonzalez (Ref. 27). All these investigators, except Mahapatra, Mahapatra, and Mishra, demonstrated arsenate removal from solutions by lime precipitation in the presence of phosphate and arsenate. The investigators agree that effective arsenic removal occurs in the pH range > 10.

Nikolaev, Masurova, Serdjuk, and Shemonaeva

Nikolaev, Masurova, Serdjuk, and Shemonaeva (1972) studied arsenic (III) and arsenic (V)

removal from wastewater solutions by using natural phosphite, reactive tris-calcium phosphate [$\text{Ca}_3(\text{PO}_4)_2$], and precipitated calcium phosphate. Their work demonstrated that arsenic could be removed from solution by natural phosphite,

reactive tris-calcium phosphate, and precipitated calcium phosphate. The authors suggested that removal was via formation of solid solutions with natural phosphite, reactive tris-calcium phosphate, and precipitated calcium phosphate. The authors did not present any quantitative data [X-ray diffraction (XRD), scanning electron microscope, etc.] to validate the existence of arsenic bearing solid solution compounds. The authors did not address the concern for long-term stability in the natural environment.

Liao

Liao (1980) received a patent for removing arsenic from aqueous mediums by adding, in the presence of phosphate, sufficient calcium hydroxide to adjust the aqueous medium pH from about 7.0 to 11.5. Liao demonstrated the removal of aqueous arsenic concentrations to below 50 Fg/L. He attributed arsenic removal to simple physical entrapment or coprecipitation complex formation. The author did not address the concern of long-term stability in the natural environment.

Mahapatra, Mahapatra, and Mishra

Mahapatra, Mahapatra, and Mishra (1987) were the first to synthesize and positively identify synthetic arsenatehydroxyapatite, $\text{Ca}_{10}(\text{AsO}_4)_6(\text{OH})_2$, (AHAP). Their research investigation was concerned with the physicochemical and thermodynamic properties of AHAP. AHAP was characterized by X-ray studies, IR spectra, electron microscopy, and thermography (TGA, DTA, and DTG). Reference was not made to arsenic removal from process or wastewater solutions.

Gonzalez

Gonzalez (1992) published a Ph.D dissertation on *Stability of Calcium Arsenate Compounds*. His precipitation experiments focused on the calcium-arsenic-phosphate-chloride system. Five variables were studied: temperature, pH, As/(As+ P) ratio, Ca/(As+ P) ratio, and total

(As+ P) concentration. The precipitates were analyzed chemically, by infrared spectroscopy, by XRD, and by thermal analysis. His test work showed the existence of arseno-apatite precipitates. The author's solubility test work deemed the precipitates unsuitable for pond disposal.

3.1.2 Modeling of Data

Thermodynamic stability (solubility) diagrams can be utilized to model the apatite-like precipitation process. To successfully model the precipitation process, it is necessary to know the free energies of formation of all solid and solution species present in the system. These data are available for all species anticipated in the present study except for the new arsenate/phosphate apatite-like compounds (these data have been determined by the present study). One must be careful to use a consistent set of free energy data values in all modeling efforts. The species and the selected free energies of formation used in this study are presented in Table 3-2. At this time, Dr. Huang's STABCAL software is the best and most appropriate thermodynamic calculational program available, and it is the program used throughout this presentation (Ref. 28).

3.1.3 Stability to Air Exposure

The success of this study was based on the formation of calcium arsenatephosphate-hydroxyapatite compounds at ambient temperatures and their relative stability in ponding environments exposed to air (containing, of course, carbon dioxide), i.e., the question is whether the hydroxyarsenatephosphate is more stable than calcium carbonate under ponding conditions and, if so, what are the proper storage conditions (pH, aqueous specie concentrations) for long-term containment of the solids.

Calcium arsenates have been shown to be quite unstable under pond storage conditions at pH values above about 8.2. The effect of carbon

dioxide on the stability of calcium arsenate (for the stoichiometric Ca/As mole ratio in calcium arsenate, i.e., 3/2) is presented in Figures 3-1 (no carbon dioxide) and 3-2 (carbon dioxide in air). Of course, under ponding conditions usually a great amount of lime is used, e.g., in developing a neutralization treatment process for the Berkeley Pit water, Chi Lu (Ref. 32) used 4.28 grams (g) of lime/liter of water (this is EPA's selected best alternative for treating Berkeley Pit water). This amount of lime reflects a Ca/As mole ratio of 6331 in the precipitation system. The stability diagrams for this condition are presented in Figures 3-3 (no air exposure) and 3-4 (air exposure included in the calculation). Note that arsenic is effectively removed from solution in the pH range of 8 to 10 but continued exposure of this system to air (thereby, exposure to carbon dioxide) would result in conversion of the calcium arsenate to calcium carbonate (as represented in Figure 3-4).

cursory attention but will be the subject of an upcoming continuation study.

Therefore, industry has concluded that simply liming a wastewater is not an appropriate removal technology if the resulting solids are to be stored in an outdoor chemical ponding environment. However, as has been demonstrated in this present study, the formation of calcium arsenatephosphatehydroxyapatites yields a stable solid for outdoor chemical pond storage.

3.2 Research Approach

The approach taken in this study consisted of the following sequences of investigation.

- C **Exploratory studies to develop a recipe** for successfully stripping arsenic from synthetic laboratory solutions. Emphasis was placed on Ca/As/P precipitation possibilities. Effective arsenic recovery was demonstrated. Secondary emphasis was placed on arsenic removal by precipitation from the Fe/As/P system. The iron system was only given

- C **Identification of precipitated apatite-like** compound stoichiometries and structures. Identification was performed using chemical digestion and Inductively Coupled Plasma (ICP) spectrometry, XRD, scanning electron microscopy with energy dispersive analysis capabilities (SEM-EDX), and secondary electron emission [X-ray photoelectron spectrometry (XPS)].
- C **Determination of the free energy of formation** of the precipitated apatite-like compounds. These data provided information that allowed for modeling the stability of the apatite-like compounds in various storage environments. The modeling effort was the basis for selecting the conditions for demonstrating long-term storage stability.
- C **Exposure** of precipitated compounds produced from synthetic solutions, from an acid mine drainage water, and from an industrial wastewater to air sparging **to validate long-term stability** against conversion to calcium carbonate.

3.3 Experimental Procedure

Details of the work plan and quality assurance (QA) plan are presented elsewhere (Ref. 33 and 1, respectively). The experimental procedures used in this study are briefly presented in Sections 3.3.1 through 3.3.4.

3.3.1 Exploratory Research in the Calcium-Arsenate-Phosphate System

The preliminary studies conducted to arrive at the *recipe* for both stripping arsenic from solution and for forming product solids that were stable to long-term pond storage were performed by two master of science candidate graduate students, Paul Miranda (Ref. 19) and Travis Orser (Ref. 20) and are summarized in Appendix A. Miranda was responsible for determining the influence of precipitation variables on the

removal of arsenic from solutions, i.e., he investigated the effect of variables: phosphate/arsenate (P/As) mole ratio, lime content, precipitation technique, and presence of metal ions on arsenic removal. Orser was responsible for determining the effect of P/As mole ratio on the solubility and structure of the product solids.

These two thesis studies were conducted to guide the project toward accomplishing the objectives stated previously in Section 2. The studies were exploratory and were not conducted under prescribed QA procedures. Therefore, the experimental results are not reported in this report. The techniques developed were used in setting up the conditions for the quality assured test work.

3.3.2 Preparation and Characterization of AHAP and APHAP compounds

Preparation

Arsenatehydroxyapatite (AHAP, no phosphate present), arsenatephosphatehydroxyapatite (APHAP) and hydroxyapatite (HAP, no arsenate present) all have similar structures. They are hexagonal and belong to the space group $P6_3/m$ (Ref. 34). AHAP was successfully prepared by Mahaprata (Ref. 26). His results have been successfully reproduced in the Montana Tech laboratory. APHAP has also been prepared in the Montana Tech laboratory using the Mahaprata technique on solutions containing both arsenate and phosphate. The final solid compound product produced depends on the initial P/As mole ratio in the starting solution.

To ensure that crystalline HAP and APHAP were formed, the precipitation was conducted by titrating arsenic solutions, phosphate solutions, and calcium solutions at prescribed rates (to establish the desired P/As mole ratio) into an elevated temperature solution. The experimental procedure is presented in Appendix B. The

Mahaprata technique was later modified to prevent carbon pick up from one of the reagent species used for pH control, i.e., ethylenediamine. The revised procedure used potassium hydroxide for pH control and is also presented in Appendix B.

Characterization

Structure determinations were made using XRD and X-ray photoelectron spectrometry. The experimental procedures used for these characterizations are presented in Appendix C.

Chemical characterization was performed using EPA SW-846 (Method 3050A) digestions (in triplicate). The digestates were analyzed by SW-846 (Method 6010A) using an ICP (Ref. 33).

3.3.3 Solubility Measurements

Once the compounds were formed, the solubility of AHAP and APHAP was determined in a controlled ionic strength solution. These measurements were necessary to determine the free energies of formation for each compound formed. The detailed experimental procedure is presented in Appendix D. Briefly, the solubility measurements were conducted as follows: 0.2 g of solid was placed in 100 cubic centimeters (cc) of 0.165 molar potassium nitrate (for controlling the ionic strength). The samples were placed in a constant temperature bath at 25.5 EC. The pH and temperature were monitored daily. A sample of the solution phase was extracted at 10, 30, and 90 days and analyzed for arsenic, calcium, and phosphorus.

The solution concentrations of calcium, arsenic, and phosphorus from the ICP analyses, along with the ionic strength of the solution were used to determine the free energy of reaction for the solubility process. A discussion of how the free energy of formation was calculated is presented in Appendix D.

3.3.4 Stability of Ambient Temperature Precipitated Solids

Toxicity Characterization Leaching Procedure (TCLP) Test

The TCLP was performed (by an outside laboratory, ACZ Laboratories) on the initial solids produced for the long-term air sparging aging tests (the nominal P/As mole ratios in the initial solutions were seven).

Long-Term Stability Test Work

To determine the response to long-term aging, a series of samples were exposed to air sparging for 6 months. Samples containing varying P/As ratios (0, 5, and 7) for each test system (pure system precipitated solids, Berkeley Pit precipitated solids, and ASARCO blow down water precipitated solids) were investigated. Precipitated solid samples were prepared in one liter high density polyethylene (HDPE) bottles and were continuously exposed to bubbling air. Solutions were monitored for pH and oxidation-reduction potential (E_H) as a function of time. Bottles were withdrawn from the test series at specified times, i.e., 0, 3, and 6 months.

Table 3-1. Arsenic removal from phosphate bearing solutions by lime additions (Ref. 17).

Sample	Moles Added ¹				pH	As, ppb, Then ²	As, ppb, Now ³	As, ppb, New ⁴
	As	P	Cl	CaO				
842	0.00062	0.0012	0	0.0088	12.65	0.5	0.64	6.4
845	0.00062	0.0012	0	0.0144	12.66	0.5	0.5	2.4
856	0.00062	0	0.0013	0.0075	12.61	< 0.02	0.1	2.0
861	0.00062	0	0.0013	0.0161	12.62	< 0.02	0.1	0.1
871	0.00062	0.0012	0.0038	0.0073	12.58	0.55		
872	0.00062	0.0012	0.0038	0.0088	12.59	0.5		
875	0.00062	0.0012	0.0038	0.0147	12.60	0.62	0.2	1.2
1. Moles added to original solution. 2. Then: Concentration 2 weeks after formation, 4 years ago. 3. Now: Same sample reanalyzed after 4 years storage. 4. New: Concentration two weeks after formation, July 1992.								

Table 3-2. Free energies of formation at 25 EC for the species used in modeling calculations.

Species	Free Energy of Formation (kcal/g-mole)	Source
Arsenic		
H ₃ AsO ₄	-183.08	MINTEQA2 (Ref. 29)
H ₂ AsO ₄ ⁻	-180.02	MINTEQA2 (Ref. 29)
HAsO ₄ ²⁻	-170.80	MINTEQA2 (Ref. 29)
AsO ₄ ³⁻	-154.98	MINTEQA2 (Ref. 29)
FeH ₂ AsO ₄ ⁺⁺	-186.6*	Huang (Ref. 28)
FeHASO ₄ ⁺	-185.3*	Huang (Ref. 28)
FeAsO ₄ [°]	-181.1*	Huang (Ref. 28)
Fe(AsO ₄) ₂ ⁻	-351.8*	Huang (Ref. 28)
Ca ₃ (AsO ₄) ₂ (Crystalline Solid)	-732.08	Nishimura (Ref. 30)
Ca ₂ H ₂ (AsO ₄) ₂ (Crystalline Solid)	-615.30	Nishimura (Ref. 30)
Ca ₃ H ₂ (AsO ₄) ₂ (Crystalline Solid)	-1347.20	Nishimura (Ref. 30)
CaH ₄ (AsO ₄) ₂ (Crystalline Solid)	-490.90	Nishimura (Ref. 30)
FeAsO ₄ ·2H ₂ O (Crystalline Solid)	-302.96*	Huang (Ref. 28)
Phosphorus		
H ₃ PO ₄	-273.10	MINTEQA2 (Ref. 29)
H ₂ PO ₄ ⁻	-270.15	MINTEQA2 (Ref. 29)
HPO ₄ ²⁻	-260.32	MINTEQA2 (Ref. 29)
PO ₄ ³⁻	-243.48	MINTEQA2 (Ref. 29)
CaHPO ₄	-396.36	MINTEQA2 (Ref. 29)
CaH ₂ PO ₄ ⁺	-404.38	MINTEQA2 (Ref. 29)
CaPO ₄ ⁻	-384.6	Nriagu (Ref. 31)

Table 3-2. Free energies of formation at 25 EC for the species used in modeling calculations (cont'd).

Species	Free Energy of Formation (kcal/g-mole)	Source
$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ (Crystalline Solid)	-2931.5	Nriagu (Ref. 31)
$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (Crystalline Solid)	-3014.29	Nriagu (Ref. 31)
$\text{FeH}_2\text{PO}_4^{++}$	-278.68	MINTEQA2 (Ref. 29)
FeHPO_4^+	-276.29	MINTEQA2 (Ref. 29)
FePO_4 (Crystalline Solid)	-274.47	Nriagu (Ref. 31)
Calcium		
Ca^{++}	-132.31	MINTEQA2 (Ref. 29)
$\text{Ca}(\text{OH})^+$	-171.80	MINTEQA2 (Ref. 29)
CaHCO_3^+	-273.92	MINTEQA2 (Ref. 29)
CaCO_3^0	-262.76	MINTEQA2 (Ref. 29)
CaSO_4^0	-313.41	MINTEQA2 (Ref. 29)
CaCO_3 (Crystalline Calcite)	-270.02	MINTEQA2 (Ref. 29)
$\text{Ca}(\text{OH})_2$ (Crystalline Solid)	-214.72	MINTEQA2 (Ref. 29)
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Crystalline Gypsum)	-430.22	MINTEQA2 (Ref. 29)
Ferric (Fe III)		
Fe^{+++}	-1.08	MINTEQA2 (Ref. 29)
$\text{Fe}(\text{OH})^{++}$	-54.77	MINTEQA2 (Ref. 29)
$\text{Fe}(\text{OH})_2^+$	-106.69	MINTEQA2 (Ref. 29)
$\text{Fe}(\text{OH})_3^0$	-152.55	MINTEQA2 (Ref. 29)
$\text{Fe}(\text{OH})_4^-$	-198.31	MINTEQA2 (Ref. 29)
$\text{Fe}_2(\text{OH})_2^{++++}$	-111.48	MINTEQA2 (Ref. 29)
$\text{Fe}_3(\text{OH})_4^{+++++}$	-221.34	MINTEQA2 (Ref. 29)
$\text{Fe}(\text{SO}_4)^-$	-364.37	MINTEQA2 (Ref. 29)
$\text{Fe}(\text{OH})_3$, (Amorphous Solid)	-164.43	MINTEQA2 (Ref. 29)
FePO_4 , (Crystalline Solid)	-274.47	Nriagu (Ref. 31)
Ferrous (Fe II)		
Fe^{++}	-18.86	MINTEQA2 (Ref. 29)
$\text{Fe}(\text{OH})^+$	-66.3	MINTEQA2 (Ref. 29)
$\text{Fe}(\text{OH})_2^0$	-104.7	MINTEQA2 (Ref. 29)
$\text{Fe}(\text{OH})_3$, (Solid)	-116.3	MINTEQA2 (Ref. 29)
$\text{Fe}_3(\text{AsO}_4)_2$, (Solid)	-421.5	Huang (Ref. 28)
Carbon		
CO_2 , (gas)	-94.25	MINTEQA2 (Ref. 29)
H_2CO_3^0	-148.91	MINTEQA2 (Ref. 29)
HCO_3^-	-140.24	MINTEQA2 (Ref. 29)
CO_3^{--}	-126.15	MINTEQA2 (Ref. 29)
* Corrected (based on Fe^{+++} free energy of formation = 1.08 kcal/g-mole).		

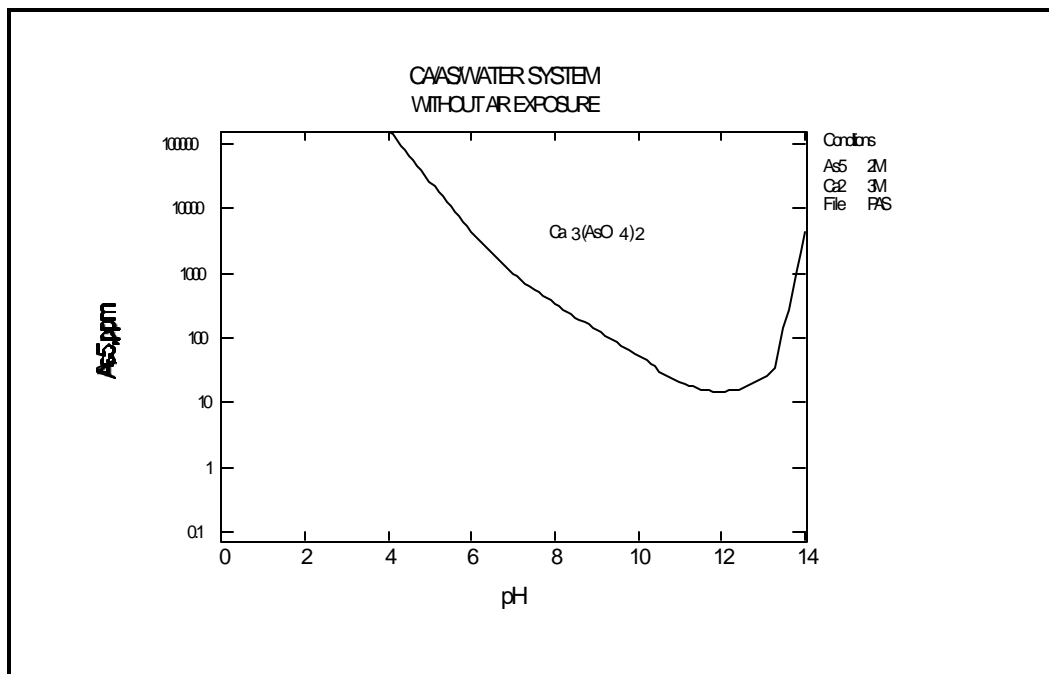


Figure 3-1. Computer generated diagram showing the stability of $\text{Ca}_3(\text{AsO}_4)_2$ at a Ca/As mole ratio of 3/2 in the absence of carbon dioxide.

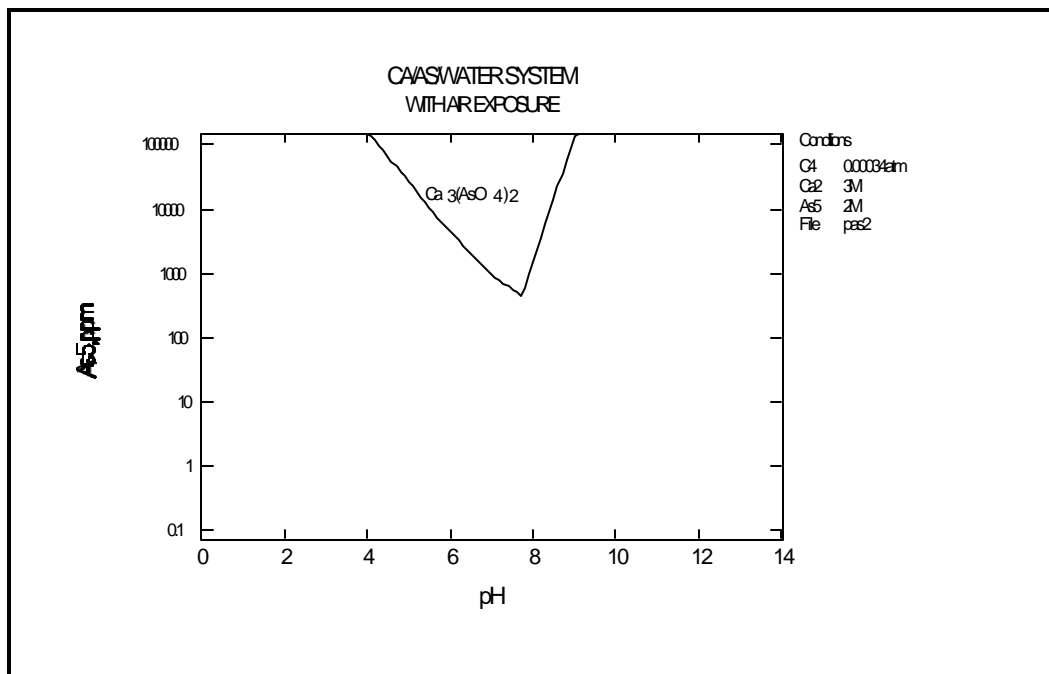


Figure 3-2. Computer generated diagram showing the stability of $\text{Ca}_3(\text{AsO}_4)_2$ at a Ca/As mole ratio of 3/2 in the presence of atmospheric carbon dioxide.

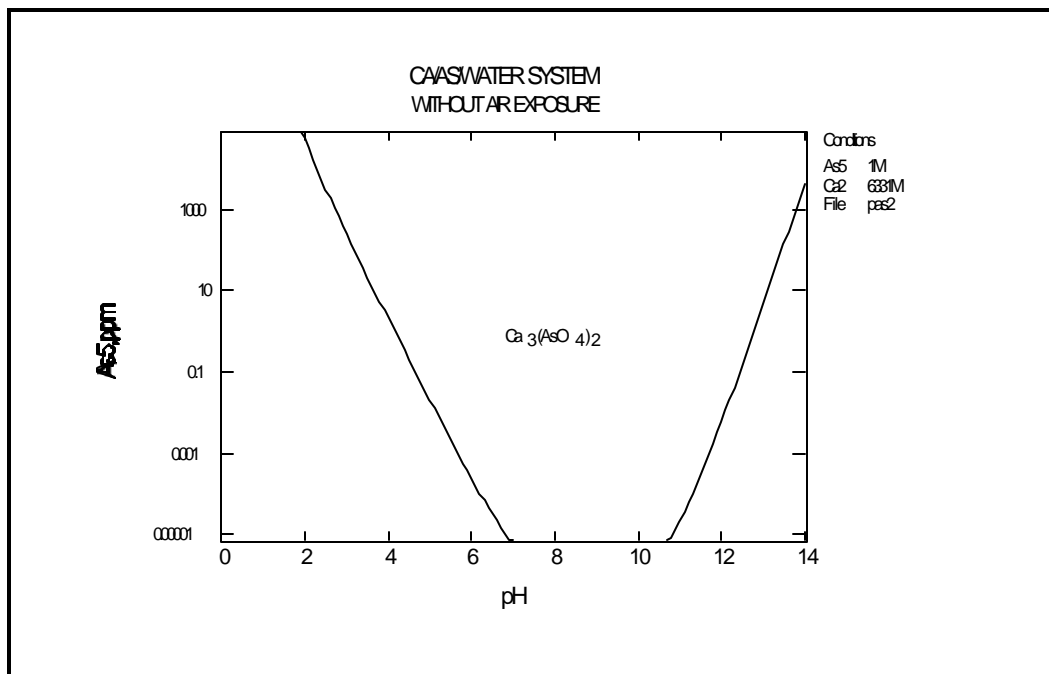


Figure 3-3. Computer generated diagram showing the stability of $\text{Ca}_3(\text{AsO}_4)_2$ at a Ca/As mole ratio of 6331 in the absence of carbon dioxide.

4. Results and Discussion

The experimental results are presented and discussed in the following sections. The experimental test work was performed by L. Twidwell and his graduate students. Four graduate students contributed to the following research results. Preliminary (exploratory) studies were conducted to arrive at a *recipe* for both stripping arsenic from solution and for forming product solids that were stable to long-term pond storage. These studies were performed by two master of science candidate graduate students, Paul Miranda (Ref. 19) and Travis Orser (Ref. 20). Miranda was responsible for determining the influence of precipitation variables on removing arsenic from solutions, i.e., he investigated the effect of variables: phosphate/arsenate (P/As) mole ratio, lime content, precipitation technique, and presence of metal ions on arsenic removal.

Orser was responsible for determining the effect of P/As mole ratio on the solubility and structure of the product solids. Two other graduate students conducted the quality assured portion of the test work, i.e., Jennifer Saran (Ref. 21) and Shannon Wilson (Ref. 22). Saran was responsible for producing AHAP and APHAP solids for the solubility test work required to determine free energies of formation for each solid compound. She also performed the long-term aging tests for the Ca/As/P water system and the Berkeley Pit water system. Wilson was responsible for performing the long-term aging tests for the ASARCO blowdown water system.

4.1 Summary of Exploratory Research Results for the Calcium-Arsenate-Phosphate System

Two thesis studies (Refs. 19, 20) were conducted

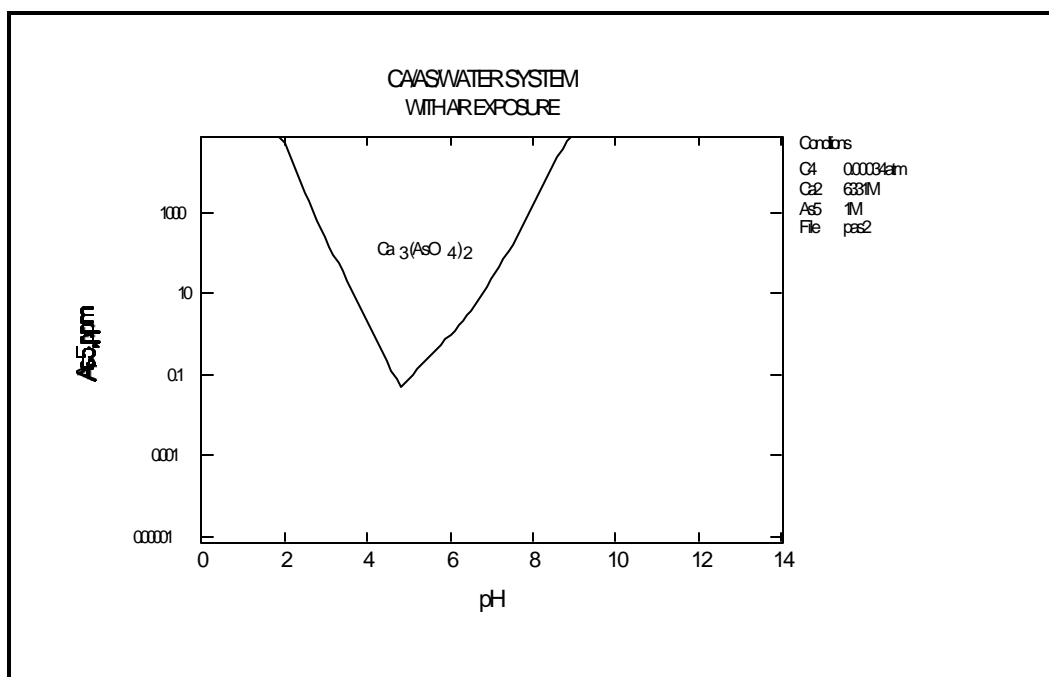


Figure 3-4. Computer generated diagram showing the stability of $\text{Ca}_3(\text{AsO}_4)_2$ at a Ca/As mole ratio of 6331 in the presence of atmospheric carbon dioxide.

to guide the project toward accomplishing the objectives stated in Section 2. The studies were exploratory and were not conducted under prescribed QA procedures. Therefore, the experimental results are not reported in this report. The techniques developed were used in setting up the conditions for the quality assured test work.

The results of the two studies showed that the presence of phosphate in an arsenate solution results in more complete removal of arsenic, the rate of precipitation is accelerated, and the amount of lime to achieve stripping arsenic (in the presence of phosphate) to below 50 ppb is greater than the stoichiometric requirement for the apatite compound $[\text{Ca}_{10}(\text{As}_x\text{P}_y\text{O}_4)_6(\text{OH})_2]$, i.e., the excess requirement was found to be 2.2 times the stoichiometric requirement for the *pure* synthetic water and 1.5 times the stoichiometric requirement for the two *real* industrial waters. The test work also demonstrated that the P/As mole ratio required to produce a compound stable against conversion to calcium carbonate when exposed to air must be equal to or greater than five (P/As mole ratios of 0, 0.2, 0.7, 1, 3, 5, 7, 10, and 20 were investigated).

Also, the exploratory test work demonstrated that arsenate does, indeed, substitute for phosphate in the apatite structure, i.e., new compounds were formed that were not reported before.

4.2 Formation and Characterization of AHAP and APHAP

4.2.1 AHAP

AHAP has the chemical formula, $\text{Ca}_{10}(\text{AsO}_4)_6(\text{OH})_2$. The compound exists in nature, and the mineral form is called Johnbaomite. AHAP was prepared in the laboratory and reported on by only one group of investigators, i.e., Mahapatra, et al. (Ref. 26). These researchers prepared the compound by precipitation from a slightly supersaturated

solution at 100 EC. They then determined the solubility product of the solid as a function of temperature. The solubility products are presented Table 4-1.

AHAP was produced in the Montana Tech laboratory using the precipitation procedure described by Mahapatra. The procedure consisted of precipitation from a nitrogen-sparged boiling solution at elevated pH from a slightly supersaturated solution. The XRD pattern for the compound formed is presented in Figure 4-1. A detailed view of the 2-theta region from 30 to 36 degrees (the region where the predominant peaks are present) is presented in Figure 4-2. The pattern is similar whether produced by the Mahapatra or the Montana Tech precipitation procedure (see Appendix B for the difference in procedures). The pattern is in reasonably close agreement with the mineral-phase Johnbaomite (which, however, is a pattern generated from a mineral specimen).

The patterns presented in Figures 4.1 and 4.2 are for AHAP precipitated from elevated temperature solutions. However, the same compound is formed by ambient temperature precipitation and ambient temperature long-term aging. For example, the XRD trace for ambient temperature precipitated sample solids shows a rather poorly developed pattern (with a cluster of poorly defined peaks at 2-theta values within the 30–36E range). The poorly developed peaks may be the result of the solid being X-ray amorphous (non-crystalline) or it may be because the solid (which may be crystalline) is of a very fine particulate size. These solids do form crystalline AHAP with time, i.e., Plessas presented XRD patterns for 4-year ambient temperature precipitated and ambient temperature aged samples that show definite crystallinity (see Figure 4-3). The aged ambient temperature sample pattern is identical to the high-temperature precipitated sample pattern.

4.2.2 APHAP

Verification of APHAP structures

Many precipitations were performed to verify that APHAP does, indeed, form. Precipitation from 95 EC solutions produced very crystalline products. The phosphorus (P) arsenic (As) ratio in the solid products depend on the P/As mole ratio in the initial solution. Several P/As mole ratios were studied in this research program, e.g., P/As mole ratios (in the initial solution) of 0, 0.2, 0.7, 3, 5, 7, 10, and no arsenic.

Hydroxyarsenate and hydroxyapatite are the two end members of a structural family series, i.e., they are both hexagonal and belong to the same space group ($P6_3/m$). When subjected to XRD, they produce the same peaks; but the peaks exist at different two-theta values, i.e., the reflective planes are the same but “d” spacings are different. This effect is illustrated in Figure 4-4. The patterns displayed in Figure 4-4 were produced from solids formed by the technique described in Appendix B. Corundum was added to the samples as an internal standard so that true alignment could be attained for the superimposed patterns.

APHAP compounds were also formed by the same precipitation technique described in Appendix B. The starting solutions contained mixtures of arsenate and phosphate. The formation of substitutional compounds was expected because the ionic radii of arsenic (+ 5 valence) and phosphorus (+ 5 valence) are similar, e.g., the atomic radius is 0.47 Å for arsenic and 0.34 Å for phosphorus (Ref. 35). The lattice parameters for HAP and AHAP are similar, e.g., for HAP: $a = 9.4176$ Å, $c = 6.8814$ Å; for AHAP: $a = 9.72$ Å, $c = 6.98$ Å (Ref. 34). An illustration of the effect of substitution of arsenate into the phosphate structure on the relative two-theta values are depicted in Figures 4-5 and 4-6.

The XRD characteristics, i.e., peak position and peak intensities, for each of the compounds formed in this study are presented in Table 4-2. XRD patterns for P/As = 0.6, 1.9, 5.7, 8.0, and 12.7 (mole ratios in the solid phase) are presented in Appendix E. The incorporation of arsenic in the apatite lattice causes a shift in the “d” spacing. The shift is further illustrated in Figures 4-7 and 4-8.

The high temperature precipitated APHAP products are very crystalline (as demonstrated by the XRD traces). Crystallinity is also very evident in photomicrographs of the apatite-like product, see Figure 4-9.

Ambient temperature precipitated products (formed when the precipitation is performed in a manner identical to the high temperature precipitated procedure) have a particulate size that cannot be resolved on a scanning electron microscope at 80,000 magnification. When subjected to XRD, the ambient temperature precipitated solids showed a cluster of peaks over the two-theta 30–36° range. This peak range is where pure hydroxyapatite and arsenatehydroxyapatite have their three major peaks. The major peaks formed in the ambient temperature products agree with the major peaks present in the high-temperature precipitated products (for the same P/As mole ratio in the initial solution), see Table 4-3. The XRD patterns for solids containing arsenic contents less than about 5% show little shift in the pattern d spacings, i.e., the d spacings are in general agreement with pure apatite. Therefore, it is not possible to conclude (from the X-ray data) that arsenate bearing apatites are formed via room temperature precipitation. It has been shown that the crystallinity is improved dramatically if the room temperature precipitated product is aged at an elevated temperature, i.e., room temperature precipitated solids when aged at 90–95 °C quickly convert to crystalline solids.

An example of this result is presented in Figure 4-10.

The demonstration that APHAP compounds form when the precipitation is conducted at elevated temperatures or when the room temperature solids are aged at elevated temperature does not necessarily mean that the compounds form at room temperature. However, room temperature formation of APHAP was demonstrated by using XPS analyses. Ambient temperature samples were prepared using the same high temperature precipitation procedure (for initial solution ratios of P/As = 0.7 and 7), except for the temperature of precipitation. The samples were citrate leached to remove calcium compounds other than the apatite-like compounds (such as calcium hydroxide). These products were subjected to XPS. XPS analyses provided a measure of atomic binding energies. The binding energy spectra for the four precipitated product solids (P/As mole ratios of 0.7 and 7 formed at ambient and 95 EC) are presented in Appendix F.

The energy for oxygen binding would be different if the room temperature solid contained different oxygen associations than the high temperature solid. For example, the oxygen binding energy for the compound CaHPO_4 would be very different from the binding energy for the compound $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (this difference has been demonstrated). Therefore, if compounds other than apatite-like solids formed during the room temperature precipitation, then different oxygen binding energy would be expected. The binding energy spectra were the same for both the room temperature and high temperature products. This result was true for both the P/As = 0.7 ratio and the P/As = 7 ratio precipitated products. Therefore, the important conclusion is that the same compounds form at room temperature and at high temperature. The major difference is the particle size and particle size distribution.

Presence of carbon in the apatite-like structure

XPS was used to determine if carbonate was incorporated into the apatite-like structure. This work was performed at the Montana State University's Chemical and Image Laboratory. Four samples were evaluated, e.g., solids produced by precipitation from solutions at 95 EC containing P/As mole ratios of 0, 5, 7, and 10. Each sample was citrate leached to ensure that the resulting product was single phase. XPS analyses were conducted on received samples (without surface cleaning by sputtering) and on surfaces cleaned by sputtering. The results are presented in Table 4-4. XPS spectra are presented in Appendix F.

Note in Table 4-4 that the majority of the carbon is present as surface adsorbed carbon. Sputtering definitely removes carbon from the sample but how effectively it removes carbon is unknown. The remaining carbon may, in fact, also be adsorbed carbon (because of incomplete removal by sputtering). Therefore, at this time, the only conclusion drawn from the XPS results is that total carbon content is as presented in Table 4-3, and no conclusion is drawn with respect to whether the carbon is structural or not.

Stoichiometry of apatite-like products

Solids produced by the Montana Tech precipitation method (Appendix B) were digested (in triplicate) and analyzed for calcium, As, and P. The resulting concentrations are presented in Table 4-5.

4.3 Solubility and Free Energy of Formation of Apatite-Like Compounds

Thermodynamic stability (solubility) diagrams can be utilized to obtain an equilibrium model for the apatite-like precipitation process. To correctly model the precipitation process, it is necessary to know the free energies of formation of all solid and solution species present in the system. Free energy of formation data are

available for all species anticipated in the present study except for the new arsenic/phosphate apatite-like compounds.

Free energy of formation data for the new APHAP compounds were obtained by making controlled solubility measurements, i.e., measurements under conditions of constant ionic strength and temperature. The solubility and free energy of formation results are presented in the following sections.

4.3.1 Solubility of Apatite-Like Compounds

Solubilities were determined for crystalline solids produced by precipitation using the Montana Tech method described in Appendix B. A wide range of compounds were produced, and the solubilities were determined. Stoichiometry and elemental composition for the compounds subjected to solubility measurements are presented in Table 4-5. Solubilities for these compounds were determined at three different times, i.e., 10, 30, and 90 days. The results are summarized in Table 4-6. Detailed individual results are presented in Appendix G. Equilibrium was established within a ten day aging time, i.e., further aging had very little apparent effect on the solubility.

As noted previously, the solids evaluated in the solubility test were all subjected to citrate leaching to ensure that only apatite-like solids were present. Saran also conducted test work on noncitrate leached solids (prepared by the Montana Tech method described in Appendix B). The results are presented in Table 4-7.

Solubility of arsenic at 25.5 EC as a function of the P/As mole ratio in the solids is presented in Figure 4-11.

Exploratory test work by Orser on solubilities of room temperature precipitated solids (using the same precipitation procedure, except for the temperature, is presented in Appendix D) at 25.5 EC are summarized in Appendix G. The arsenic solubilities were very similar to the high temperature precipitated products at the higher P/As mole ratio.

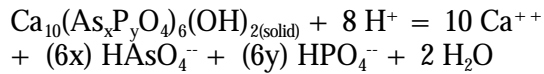
4.3.2 Standard Free Energy of Formation of Apatite-Like Compounds at 25.5 EC

The solution concentrations of calcium (Ca), As, and phosphorus from solubility measurements, along with the ionic strength of the solution were used to determine the free energy of reaction for the solubility process. A discussion of how the

free energies of formation were calculated from solubility data is presented in Appendix D.

Briefly, the procedure consists of the following steps:

Solubility data for As, P, and Ca; pH; and solution ionic strength were used to calculate the activity coefficients (γ) and then the activities for each of the species specified in the following reaction



The activity of each specie was calculated, i.e., activity = γ [concentration].

The experimental free energy for the reaction was calculated, i.e.,

$$\gamma G_{\text{Reaction}} = -RT \ln[(\text{activity of the product species} / \text{activity of the reactant species})]$$

where

$$\begin{aligned} \text{activity of product species} &= (\gamma_{\text{HPO}_4^{--}})^{6y} (\gamma_{\text{HAsO}_4^{--}})^{6x} (\gamma_{\text{Ca}^{++}})^{10} \\ \text{activity of reactant species} &= (\gamma_{\text{H}^+})^8 \end{aligned}$$

The free energy of the products was calculated, i.e.,

$$\gamma G_{\text{Products}} = \text{summation of the free energies of formation for all the product species, e.g.,}$$

$$\gamma G_{\text{Products}} = 10 \gamma G_{\text{Ca}^{++}} + 6y \gamma G_{\text{HPO}_4^{--}} + 6x \gamma G_{\text{HAsO}_4^{--}} + 2 \gamma G_{\text{H}_2\text{O}}$$

The free energies of formation used in this study were:

H ₂ O	-56.675 kilocalories per gram-mole (kcal/g-mole)
HasO ₄ ⁻⁻	-170.82
HPO ₄ ⁻⁻	-260.34

Ca⁺⁺

-132.31

The standard free energy of formation for the APHAP compound was then calculated:

$$\gamma G_{\text{(Formation of APHAP)}} = \gamma G_{\text{Products}} - \gamma G_{\text{Reaction}}$$

Standard free energy of formation at 25.5 EC for the individual apatite-like compounds are presented in Table 4-8. Note that the literature value for hydroxyapatite (Ref. 31) agrees very well with the value determined experimentally by this study.

A comparison of free energy of formation values at 25.5 EC for 95 EC precipitated citrate leached and noncitrate leached solids and for ambient temperature precipitated noncitrate leached solids are presented in Table 4-9.

These standard free energies of formation allow for modeling the actual precipitation systems (discussed in Section 9, Conclusions). The free energy of formation varies linearly with mole ratio of arsenic to moles of arsenic plus phosphorus, i.e., the mole fraction of arsenic with respect to arsenic plus phosphorus. This result is depicted graphically in Figure 4-12. The multiple regression coefficient is 0.9989. This result has important theoretical significance, i.e., the compound free energies lie on an almost perfectly straight line (with respect to the arsenic to arsenic plus phosphate mole ratio), which indicates that these compounds show almost ideal behavior. The compounds appear to be ideal solid solutions that form between pure AHAP and pure HAP. The relative solubilities of each of the apatite-like compounds are depicted graphically in Figure 4-13.

4.4 Stability of Apatite-Like Precipitated Solids

4.4.1 TCLP for Apatite-Like Precipitated Products

A waste is designated a Resource Conservation and Recovery Act (RCRA) hazardous waste if it fails the EPA TCLP test. Three samples were

subjected to the TCLP test. The samples evaluated were newly precipitated solids formed by the *recipe* for the individual system being studied, e.g., pure system precipitation conditions consisted of P/As mole ratio of 7 and a Ca/(As+ P) mole ratio of 3.67 (this is 2.2 times the stoichiometric requirement for formation of the APHAP compound); Berkeley Pit water precipitation conditions consisted of P/As mole ratio of 7 and a Ca/(As+ P+ SO_4^{--}) ratio of 2.5; and ASARCO water precipitation conditions consisted of P/As mole ratio of 7 and a Ca/(As+ P+ SO_4^{--}) ratio of 2.5.

The TCLP results are presented in Table 4-10. All samples passed the test for all elements, i.e., all element concentrations were less than one hundred times the drinking water standard; therefore, the solids are deemed not to be a RCRA hazardous material. The only questionable value is for Berkeley Pit water selenium extraction. The TCLP result for selenium was reported to be < 2 milligrams per liter (mg/L); the characteristic level for selenium is 1 mg/L.

4.4.2 Long-Term Stability in Air

To determine the response to long-term aging, a series of samples were exposed to air sparging for 6 months. Samples containing various P/As mole ratios (0, 5, and 7) for each test system (pure synthetic precipitated solids, Berkeley Pit precipitated solids, and ASARCO blow down water precipitated solids) were investigated. Precipitated solid samples were prepared in 1-liter HDPE bottles and were continuously exposed to bubbling air. Solutions were monitored for pH and E_H as a function of time. Bottles were withdrawn from the test series at specified times, i.e., 0, 3, and 6 months.

Solutions were analyzed by ICP, and solids were digested and analyzed by ICP (to determined solid stoichiometry) and characterized by XRD

(to observe whether aging improved crystallinity).

to be continued for longer times to ensure that true stability does exist.

Experimental results for up to and including 6 month aging tests are summarized in Tables 4-11, 4-12, and 4-13. Detailed individual results are presented in Appendix H including concentration values for calcium, iron, copper, zinc, and sulfur.

The conclusions drawn from the long-term aging data are summarized below:

Pure System

- C The AHAP compound (no phosphate present) was not stable, i.e., arsenic was initially removed from the solution (to 57.7 ppb) but was subsequently released back to the solution with aging time to rather high concentrations (e.g., at 6 months the arsenic concentration was 85,100 ppb).
- C The APHAP compounds (phosphate present in the solid) showed very low solubilities at all times. For the P/As = 5 and 7 test systems, the arsenic solubility was < 50 ppb for all times investigated. The goal of this project was to strip and maintain the arsenic concentration at < 50 ppb (less than the current U.S. drinking water standard).
- C The arsenic solubility for the solids produced by precipitating from a P/As = 7 solution was < 10 ppb. Ten ppb is the current drinking water standard in Japan and Germany.

Berkeley Pit Water

- C All analyses showed that the arsenic concentration was < 50 ppb for all test conditions. There does appear to be a trend of increasing arsenic release with aging time for all the P/As = 0 samples.
- C The phosphate bearing solids did not appear to be changing with aging time. These tests need

ASARCO

- C The phosphate free test samples were definitely not stable to air sparging with time. Arsenic was initially removed from the solution (to 2800 ppb) but was subsequently released back to the solution with aging time to rather high concentrations (e.g., at 6 months the arsenic concentration was 601,000 ppb).
- C The phosphate bearing solid samples showed excellent stability with time. All sample solubilities were < 50 ppb.

Solution pH is a measurable variable that depicts solid stability, i.e., if the solid apatite-like compound is more stable than calcium carbonate then the pH of the solution will remain above a pH of about 8.2. For the apatite-like compounds to be stable, the incongruent pH must lie considerably above 8.2. If calcium carbonate is more stable than the apatite-like phase then the apatite-like phase will be converted to carbonate and the pH of the system will decrease (as air, containing carbon dioxide, is sparged into the slurry) with time. Therefore, if the pH does not appreciably decrease with time then the solid apatite-like phase is more stable than calcium carbonate and the lack of pH decrease is a confirmation of the stability of the apatite-like compounds. This result is illustrated in Figure 4-14. Note that the pH of the solution containing non-phosphorus bearing arsenate solids has dropped dramatically with time, while the pH of the phosphate/arsenate bearing solid/liquid system has remained relatively constant. Additional pH/time plots (for Berkeley Pit and ASARCO waters) are presented in Appendix H.

4.4.3 Precipitated Product Properties

The solubility of solids produced by precipitation from solutions containing a P/As mole ratio of seven was shown to be the lowest of all the precipitated solids tested. Therefore, emphasis was subsequently placed on determining the elemental make-up of these solids, the TCLP

response of these solids (reported in Section 4.4.1), and the physical and structural properties of these solids. The properties are discussed (with emphasis on the 6-month aged air exposed precipitated solids) and are summarized in the following sections.

4.4.3.1 Elemental Content

The elemental concentrations in the 6-month aged product were determined. The results are presented in Table 4-14.

4.4.3.2 X-Ray Diffraction (XRD)

Newly precipitated solids and 6-month aged solids (for the pure synthetic, the Berkeley Pit, and the ASARCO systems) were subjected to XRD analyses. Each system is discussed separately.

Pure System (Detailed data in Appendix I)

Pure system samples that were aged under air exposure included solids produced by precipitating from solutions containing nominal P/As mole ratios of 0, 5, 5 duplicate, and 7.

P/As = 0

XRD patterns for the room temperature P/As = 0 precipitated solids (no phosphorus present) are presented in Appendix I. The room temperature precipitated products were crystalline, i.e., the X-ray patterns were distinct. There was no obvious changes in the XRD patterns for the initially precipitated solids and those aged for six months. The major peak positions in the two-theta region (30–36E) were similar to the 95 EC precipitated peak positions. Therefore, the conclusion is that the room temperature precipitated products were, indeed, apatite-like compounds. The room temperature precipitated products showed additional unidentified peaks not present in the high temperature precipitated product, i.e., the room temperature products contained the AHAP compound and other additional unidentified compounds (they were not calcium hydroxide or calcium carbonate).

P/As = 5, 7

Room temperature precipitated products showed that a large portion of the solid was calcium hydroxide. This was expected since the precipitation was performed using greater amounts of lime than is required to satisfy the stoichiometry. The characteristic cluster of peaks are evident in the two-theta range 30–36E, but definition of the individual peaks is not sufficient to state that the same compounds formed at room temperature as at high temperature. It is anticipated that with further aging, the characteristic peaks will become evident. Citrate leaching to remove all extraneous compounds from the mixture was not conducted. With hindsight, these tests should have been conducted to prove that the room temperature apatite-like compounds were, indeed, the same as formed from high temperature precipitation. Citrate leaching of these solids will be conducted during the continuation study beginning in May 1997.

Berkeley Pit System

Berkeley Pit system samples were aged under air exposure included solids produced by precipitating from solutions containing nominal P/As mole ratios of 0, 5, and 7. The XRD results showed that the major phase formed (which predominates the pattern) was gypsum. Useful data concerning the potential formation of apatite-like compounds was not obtained from X-ray analysis.

ASARCO System

ASARCO system samples that were aged under air exposure included solids produced by precipitating from solutions containing nominal P/As mole ratios of 0, 5, and 7. The XRD results showed that the major phase (which predominates the pattern) initially present was calcium hydroxide. The 2-theta (at 32–36E) cluster was present but without distinct definition. With time, the samples showed conversion of the calcium hydroxide to calcium carbonate with

increased definition of the crystallinity in the 2-theta cluster region. Further aging is necessary to ensure that crystalline APHAP products continue to develop.

4.4.3.3 Particle Size and Particle Size Distribution

The particle size of room temperature precipitated apatite-like solids was much finer than for the high-temperature precipitated APHAP solids. Individual crystals could be easily resolved for the high temperature precipitated solids. The crystallite size range was approximately 1–2 micrometers (1000–2000 nanometers). A SEM-EDX photomicrograph of the well developed crystalline solid was presented previously in Figure 4-9.

The Malvern Instruments Laboratory determined the particle size of room temperature precipitated solids ($P/As = 7$, $Ca/(As + P) = 3.7$) by photon correlation spectroscopy. The particle sizes and particle size distribution are presented in Table 4-15. The mean particle size (depending on the type of response measurement) was between 140–300 nanometers.

4.4.3.4 Settling Properties

The settling characteristics of the precipitated solid products are very important with respect to designing solid/liquid separation unit operations, i.e., filtering devices, clarifiers, and thickeners. The settling characteristics of solids were determined by the Kynch procedure (Ref. 37).

Settling rates for APHAP, Berkeley Pit, ASARCO precipitated air-aged solids

The settling characteristics were determined for the *recipe* precipitated products from each of the three test waters. All the solids were prepared from solutions containing initially a P/As mole ratio of 7. A sample was taken from each aging test series (from the air exposure bottle test series) after 6-months aging time. The experimental results are summarized in Figure

4-15. The settling rates presented in Figure 4-15 are based on using a cationic flocculant, i.e., 80 cc of 0.01% Superfloc 330 for the pure synthetic system and 50 cc of 0.01% Superfloc for the Berkeley Pit and ASARCO systems. The supernatant solution after the settling tests all appeared clear. The complete data set are in Appendix J.

These data illustrate that (even though the particle sizes are relative small) effective solid/liquid separations are appropriate. The data also can be used to design a thickener, i.e., the diameter and volume can be specified using these data.

Specific gravities for APHAP, Berkeley Pit, ASARCO precipitated air-aged solids

Specific gravity was determined by the weight/pycnometer technique. The specific gravity for each of the $P/As = 7$, 0- and 6-month aged products are in Table 4-16. The products in this table include the precipitated apatite-like solid products and calcium hydroxide solid products.

4.5 Summary of Exploratory Research Results for the Iron-Arsenate-Phosphate System

4.5.1 Background

Excellent results were obtained in the $Ca/As/P$ system with respect to arsenic removal from solution and for stability of the resultant compounds when exposed to air sparging. The concept of substitution of arsenate for phosphate in mineral structures (with dramatically increased stability in tailings-pond-type storage areas) was confirmed by the test work performed in the $Ca/As/P$ system. Thus, it is likely that arsenate substitution in other phosphate minerals may result in compounds that are stable for long-term outdoor storage. The $Fe/As/P$ water system is a likely candidate system.

Therefore, the Fe/As/P system was investigated. Only exploratory test work was conducted during the present study.

The theoretical basis for considering the Fe/As/P system is depicted in Figure 4-16, i.e., the solubility diagram for ferric phosphate and ferric arsenate. Note in the diagram that the solubility of ferric phosphate is many orders of magnitude less than the solubility of ferric arsenate over the pH range 2–6 (at ~ 50 ppb). If arsenate can be effectively substituted into the ferric phosphate structure, the solubility of arsenic for a $\text{Fe}(\text{As}_x\text{P}_y)\text{O}_4$ compound (FAP) should be considerably less than from ferric arsenate. Also, if the ferric arsenate phosphate solid solution compound can be formed, then it should be stable against carbon dioxide in air because ferric iron does not form a solid carbonate phase.

Another question (in addition to the substitution question) that needs to be answered is whether the FAP compound would form in preference to ferrihydrite (with arsenic being removed by adsorption instead of compound formation). Thermodynamically, ferric phosphate is the stable phase at pH levels in the near neutral region (pH 5–6). This is shown by the E_{H} /pH diagram in Figure 4-17. However, an amorphous ferric phosphate (with arsenic adsorption) may occur during actual precipitation similar to what happens in precipitation from a nonphosphate system, i.e., arsenic adsorption on ferrihydrite.

The Fe/As/P water system (if substitution of arsenate does occur) has several advantages over the Ca/As/P system, e.g., less neutralization of acid mine water would be required, i.e., instead of precipitating at pH levels of 10–12, precipitation could be performed at near neutral pH levels (pH = 5–8). Therefore, less lime would be required.

Iron is often present in acid mine waters. Therefore, the precipitant cation is already present. Again, less lime would be required.

4.5.2 Results and Discussion

Miranda (Ref. 19) investigated two approaches for the formation of FAP, i.e., precipitation from a ferric solution and precipitation from a ferrous solution; both at 95 EC. Refer to his thesis for detailed information.

The precipitation from the ferric solution (at a P/As mole ratio in the starting solution of one, pH 4, 95 EC) resulted in an amorphous XRD pattern; even when the slurry was aged for up to 40 days at 95 EC. Therefore, the emphasis of the exploratory work was shifted to the ferrous system.

The reason for investigating the ferrous system was based on the concept that ferrousarsenatephosphate (F_2AP) may form as a crystalline product that upon air aging (of the slurry) could be converted to ferricarsenatephosphate (FAP). Note in the previous E_{H} /pH diagram (Figure 4-16) that ferrous phosphate has a wide range of stability, i.e., its formation should be possible under reducing conditions over the pH range of 2–14.

Two P/As ratios, 5 and 1, were investigated. The conditions for the precipitation experiments were: 95 EC, P/As mole ratio in the starting solution = 1 or 5, pH~ 8. The solids produced by the precipitations were crystalline and were identified to be lipscombite, $\text{Fe}_3[\text{PO}_4]_2(\text{OH})_2$. The lipscombite XRD 2-theta values were slightly shifted indicating structural substitution, see Figure 4-18. The chemical make-up of the solid from the P/As = 5 precipitation was 38.7% iron, 5.6% arsenic, and 16.6% P; from the P/As = 1 precipitation was 35.0% iron, 9.4% arsenic and 15.5% phosphorus.

4.5.3 Future Work

The concept of substituting arsenate into a ferric phosphate structure to gain stability appears to warrant further attention. Twidwell (Ref. 37) was funded by the MWTP program to continue study of this system. One graduate student will begin studying this system in June 1997.

Table 4-1. AHAP solubility products (Mahapatra, Ref. 26).

T EC	K_{sp}	$\Delta G_{\text{reaction}}$ kcal/g-mole
35	4.0E-91	127.40
40	2.7E-91	129.72
45	2.1E-91	131.95
50	1.2E-91	134.38

Table 4-2. XRD characteristics of apatite-like compounds.

HAP		AHAP P/As = 0.1		APHAP P/As = 0.6		APHAP P/As = 1.9		APHAP P/As = 5.7		APHAP P/As = 8.0		APHAP P/As = 12.7	
I/I ₀	d	I/I ₀	d	I/I ₀	d	I/I ₀	d	I/I ₀	d	I/I ₀	d	I/I ₀	d
1.00 (1.00)	2.8082 (2.8140)	1.00	2.8779	1.00	2.869	1.00	2.8436	1.00	2.8318	1.00	2.8212	1.00	2.8215
0.63 (0.60)	2.7168 (2.7200)	0.67	2.8335	0.94	2.803	0.76	2.7995	0.80	2.7916	0.88	2.792	0.86	2.7963
0.62 (0.60)	2.7732 (2.7780)	0.63	2.7909	0.92	2.869	0.66	2.7562	0.65	2.7294	0.61	2.7252	0.62	2.7351
0.42 (0.40)	3.4311 (3.4400)	0.39	2.6863	0.69	3.4748	0.44	1.8573	0.50	1.8513	0.60	1.8491	0.53	1.8505
0.44 (0.40)	1.8416 (1.8410)	0.38	1.8803	0.49	1.8683	0.42	1.9652	0.39	1.7299	0.43	1.9519	0.32	1.9564
0.32 (0.25)	2.6272 (2.6310)	0.33	3.9729	0.29	1.9834	0.39	2.656	0.39	1.9533	0.38	2.6428	0.30	2.6463
0.3 (0.25)	1.7190 (1.7220)	0.29	1.9874	0.24	2.6722	0.26	1.7317	0.19	1.4577	0.35	2.2697	0.26	2.2321
Seven most intense lines. Literature values for HAP (Ref. 34) in parenthesis. P/As refers to the mole ratio in the solid phase (See Table 4-4).													

Table 4-3. Comparison of XRD peak position and intensity ratio for 95 EC and ambient temperature precipitated apatite-like products.

APHAP P/As = 8.0		APHAP P/As = 8.0		APHAP P/As = 12.7		APHAP P/As = 12.7		APHAP P/As = 12.7	
95 EC		Ambient		95 EC		95 EC		Ambient	
I/I ₀	d	I/I ₀	d	I/I ₀	d	I/I ₀	d	I/I ₀	d
1.00	2.8212	1.00	2.8196	1.00	2.8215	1.00	2.8126	1.00	2.8117
0.88	2.792	0.76	2.7733	0.86	2.7963	0.76	2.782	0.89	2.77
0.61	2.7252	0.51	2.7375	0.62	2.7351	0.63	2.7205	0.67	2.7408
0.60	1.8491			0.53	1.8505	0.61	1.8421		
0.43	1.9519			0.32	1.9564	0.47	1.9461		
0.38	2.6428			0.30	2.6463	0.31	2.6335		
0.35	2.2697			0.26	2.2321				
P/As refers to the mole ratio in the solid.									

Table 4-4. Effect of sputtering on final carbon content of apatite-like compounds.

Sample	Description	Carbon Content, %	
		nonsputter	sputter
5-060396-95-1	APHAP, P/As in the solid = 5.7	10.0	3.3
7-060396-95-2	APHAP, P/As in the solid = 8.0	9.8	2.7
10-060396-95-1	APHAP, P/As in the solid = 12.7	11.6	2.4

Table 4-5. Stoichiometry and elemental concentration of apatite-like compounds.

Investigator	P/As mole ratio		$\text{Ca}_w(\text{As}_x\text{P}_y\text{O}_z)(\text{OH})_z$				Element concentration, %		
	Nominal in initial solution	Final solid	w	x	y	z	As	P	Ca
Saran	0	0.06 ± 0.01	10	0.94	0.06	6	28.6 ± 0.7	0.8 ± 0.1	31.6 ± 0.5
Orser (non-QA)	0.2	0.6 ± 0.1	10	0.63	0.37	6	18.5 ± 2.1	4.5 ± 0.2	29.8 ± 3.6
Orser (non-QA)	0.7	1.9 ± 0.0	10	0.35	0.66	6	13.7 ± 0.4	10.8 ± 0.3	38.6 ± 1.1
Saran	5	5.7 ± 0.4	10	0.15	0.85	6	5.9 ± 0.3	14.0 ± 0.3	37.0 ± 0.6
Saran	7	8.0 ± 0.2	10	0.11	0.89	6	4.4 ± 0.2	14.0 ± 0.3	37.2 ± 0.9
Saran	7	7.9 ± 0.1	10	0.11	0.89	6	4.3 ± 0.2	14.1 ± 0.8	36.2 ± 1.7
Saran	10	12.7 ± 0.2	10	0.01	0.99	6	2.9 ± 0.1	15.1 ± 0.4	37.7 ± 0.5
Saran	No As	-	10	0.00	1.00	6	0.1 ± 0.02	17.7 ± 2.3	37.0 ± 4.8
Niagru (Ref. 31)	No As	-	10	0.00	1.00	6	0	19	39.9
Precipitated solids were subjected to citrate leaching (Appendix K) to ensure that only the apatite-like compounds were present. All reported values are an average of triplicate digestions and analyses (except the P/As = 0 data are an average of duplicate digestions). Saran (Ref. 21). Orser (Ref. 20).									

Table 4-6. Summary of apatite-like compound solubilities at 25.5 EC.

Stoichiometry	P/As in init. solu.	P/As in final solid	Solubility, mg/L											
			10 days				30 days				90 days			
			pH	As	P	Ca	pH	As	P	Ca	pH	As	P	Ca
$\text{Ca}_{10}(\text{As}_{0.94}\text{P}_{0.06}\text{O}_4)_6(\text{OH})_2$	0	0.06 ± .01	10.2 ± .1	22.0 ± 2.6	0.4 ± .0	27.8 ± 1.0								
$\text{Ca}_{10}(\text{As}_{0.63}\text{P}_{0.37}\text{O}_4)_6(\text{OH})_2$ (non-QA)	0.2	0.6 ± .1	7.9 ± .1	26.9 ± 1.6	0.7 ± .5	22.2 ± .8								
$\text{Ca}_{10}(\text{As}_{0.35}\text{P}_{0.65}\text{O}_4)_6(\text{OH})_2$ (non-QA)	0.7	1.9 ± .0	7.5 ± .1	11.5 ± .8	1.1 ± .2	12.0 ± .7								
$\text{Ca}_{10}(\text{As}_{0.15}\text{P}_{0.85}\text{O}_4)_6(\text{OH})_2$	5	5.74 ± .43	7.5 ± .2	3.4 ± .8	1.2 ± .3	9.7 ± 2.4	7.6	2.1	2.0	9.1	7.8	4.1	1.2	8.3
$\text{Ca}_{10}(\text{As}_{0.11}\text{P}_{0.89}\text{O}_4)_6(\text{OH})_2$	7	7.98 ± .18	7.5 ± .2	2.6 ± .9	1.8 ± 1.1	12.0 ± 4.2	7.6 ± .0	1.9 ± .2	2.0 ± .1	8.8 ± .4	7.7 ± .1	2.6 ± .0	1.2 ± .2	9.1 ± .4
$\text{Ca}_{10}(\text{As}_{0.07}\text{P}_{0.93}\text{O}_4)_6(\text{OH})_2$	10	12.70 ± .20	7.2 ± .2	2.6 ± 1.0	2.3 ± .4	14.8 ± 7.1	7.7 ± .1	2.2 ± .6	2.2 ± .5	6.4 ± .7	7.8 ± .0	2.2 ± .0	1.1 ± .0	9.4 ± .3
$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	No As	--	7.1 ± .1	1.5 ± .3	3.0 ± .1	12.6 ± .3								
P/As ratios are mole ratios. The data presented in this table are average values. See Appendix G for detailed solubility data.														

Table 4-7. Solubility results for citrate leached APHAP compounds and noncitrate leached APHAP compounds.

Nominal P/As in init. solu.	Solubility, mg/L							
	10 days: citrate leached				10 days: noncitrate leached			
	pH	As	P	Ca	pH	As	P	Ca
5	7.5± 0.2	3.4± 0.8	1.2± 0.3	9.7± 2.4	7.5± 0.1	2.2± 0.2	1.5± 0.2	3.5 ± 0.6
7	7.5± 0.2	2.6 ± 0.9	1.8± 1.1	12.0 ± 4.2	7.5± 0.1	1.7± 0.1	1.6± 0.1	4.2± 0.4
10	7.2± 0.2	2.6± 1.0	2.3± 0.4	14.8± 7.1	7.3± 0.2	1.5± 0.1	1.5± 0.0	2.9± 0.2
P/As ratios are mole ratios. Data presented in this table are average values. See Appendix G for detailed solubilities.								

Table 4-8. Standard free energy of formation of apatite-like compounds at 25.5 EC.

Compound Stoichiometry) $G^{\circ}_{(Formation)}$	
	kcal/g-mole	kJ/g-mole
$Ca_{10}(As_{0.94}P_{0.06}O_4)_6(OH)_2$	-2,466.1 ± 3.7	-10318.2 ± 15.5
$Ca_{10}(As_{0.63}P_{0.37}O_4)_6(OH)_2$ (non-QA)	-2671.0 ± 16.0	-11175.4 ± 66.9
$Ca_{10}(As_{0.34}P_{0.66}O_4)_6(OH)_2$ (non-QA)	-2826.9 ± 1.6	-11827.7 ± 6.7
$Ca_{10}(As_{0.15}P_{0.85}O_4)_6(OH)_2$	-2932.4 ± 9.3	-12269.2 ± 38.9
$Ca_{10}(As_{0.11}P_{0.89}O_4)_6(OH)_2$	-2952.4 ± 4.7	-12352.8 ± 19.7
$Ca_{10}(As_{0.07}P_{0.93}O_4)_6(OH)_2$	-2973.2 ± 4.2	-12439.9 ± 17.6
$Ca_{10}(PO_4)_6(OH)_2$	-3014.0 ± 4.2	-12610.6 ± 17.6
$Ca_{10}(PO_4)_6(OH)_2$, synthetic (Ref. 31)	-3014.3	-12611.8
The standard free energies of formation presented in this table are average values, i.e., a free energy of formation was calculated for each solubility measurement, and then the average was determined for each compound stoichiometry. All samples were citrate leached (see Appendix K for procedure) to ensure that only a single solid phase was present during the solubility measurements. See Appendix L for a detailed tabulation of all free energy of formation values.		

Table 4-9. Comparison of free energy of formation (at 25.5 EC) of apatite-like compounds for various treatments.

Compound Stoichiometry	Free energy of formation, kcal/g-mole		
	Citrate leached ¹	Noncitrate leached ¹	Noncitrate leached ²
$Ca_{10}(As_{0.94}P_{0.06}O_4)_6(OH)_2$	-2,466.1 ± 3.7		
$Ca_{10}(As_{0.63}P_{0.37}O_4)_6(OH)_2$ (non-QA)	-2671.0 ± 16.0		
$Ca_{10}(As_{0.34}P_{0.66}O_4)_6(OH)_2$ (non-QA)	-2826.9 ± 1.6	-2821.2 ± 2.5	-2827.5 ± 5.2
$Ca_{10}(As_{0.15}P_{0.85}O_4)_6(OH)_2$	-2932.4 ± 9.3	-2939.1 ± 1.5	
$Ca_{10}(As_{0.11}P_{0.89}O_4)_6(OH)_2$	-2952.4 ± 4.7	-2959.3 ± 1.8	
$Ca_{10}(As_{0.07}P_{0.93}O_4)_6(OH)_2$	-2973.2 ± 4.2	-2985.6 ± 0.4	
$Ca_{10}(PO_4)_6(OH)_2$	-3014.0 ± 4.2		
$Ca_{10}(PO_4)_6(OH)_2$, synthetic (Ref. 31)	-3014.3		
The standard free energies of formation presented in this table are average values, i.e., a free energy of formation was calculated for each solubility measurement, and then the average was determined for each compound stoichiometry. See Appendix L for a detailed tabulation of all free energy of formation values. ¹ Solids were formed by precipitating from a 95 EC solution. ² Solids were formed by precipitating from an ambient temperature solution.			

Table 4-10. TCLP results for room temperature precipitated APHAP solids.

Sample	Description	TCLP Extract Concentration, mg/L							
		As	Ba	Cd	Cr	Pb	Hg	Se	Ag
APHAP-221497P/As7	Synthetic Solu. Ppt. Solids	< 0.2	0.009	< 0.02	0.02	< 0.04	< 0.0002	< 0.04	< 0.006
BERK-3597P/As7	Berkeley Pit Water Ppt. Solids	< 2	0.02	< 0.2	< 0.6	< 2	< 0.0002	< 2	< 0.3
ASARCO-3597P/As7	ASARCO Blow-down Water Ppt. Solids	2.8	< 0.003	1.1	0.14	< 0.04	0.0417	0.25	< 0.006

All TCLP tests were conducted by ACZ Laboratories in accordance with EPA ICP protocol except for the BERK (BPIT) water precipitated solids.

The BPIT TCLP test was conducted using only 50 g of solid. The solid/liquid ratio was maintained the same as in the standard protocol.

The ACZ Laboratories method detection limits values in mg/L were:

APHAP; As 0.2, Ba 0.003, Cd 0.02, Cr 0.01, Pb 0.04, Hg 0.0002, Se 0.04, Ag 0.006

BERK; As 2, Ba 0.003, Cd 0.2, Cr 0.6, Pb 2, Hg 0.0002, Se 2, Ag 0.3

ASARCO; As 0.2, Ba 0.003, Cd 0.02, Cr 0.01, Pb 0.04, Hg 0.0004, Se 0.04, Ag 0.006.

Characteristic Element TCLP limits in mg/L: As 5, Ba 100, Cd 1, Cr 5, Pb 5, Hg 0.2, Se 1, Ag 5.

Table 4-11. Summary of experimental results for long-term air sparging of room temperature precipitated apatite-like products: pure system.

Sample Description		Concentration, µg/L	
Nominal P/As mole ratio in the initial solution	Months aged	Arsenic	Phosphorus
Starting Water		1000000.0	0.0
0	0	57.7	4.4
	1	42110 ²	< DL
	3	78100 ²	9312
	6	85090 ± 170	
5	0	6.6	4.7
	1	< IDL	19.1
	3	34.3	21.0
	6	9.8 ± 9.8	1.7 ± 1.3
5 Duplicate	0	14.5 ± 7.9	32.4 ± 16.3
	6	1.0 ± 2.1	2.7 ± 1.5
7	0	1	1
	1	< IDL	< IDL
	3	4.9	11.1
	6	3.4 ± 1.0	4.0 ± 0.8

Reported sample values are averages based on one to three analyses, see Appendix H for detailed individual results including values for Ca, Fe, Cu, Zn, and S.

¹Sample P/As = 7 at time 0 was rejected, see Appendix H.

²QA performed using a Varian 110 ICP.

QA performed using a Perkin Elmer Optima ICP.

IDL (for Perkin Elmer Optima ICP) for As = 1.4 ppb; P = 2 ppb; and Ca = 2.9 ppb.

IDL (for Varian 110 ICP) for As = 44 ppb; P = 17 ppb; and Ca = 250 ppb.

Table 4-12. Summary of experimental results for long-term air sparging of room temperature precipitated apatite-like products: Berkeley Pit system.

Sample Description		Concentration, µg/L	
		Arsenic	Phosphorus
Starting Water		44045 ¹	638 ¹
Nominal P/As mole ratio in the initial solution	Months		
0	0	14.2	52.7
	3	21.9	17.7
	6	35.5± 3.8	18.1± 1.2
5	0	14.6	53.0
	3	19.7	18.9
	6	17.9±1.5	20.4±1.0
5 Duplicate	3	18.8	13.7
7	0	< IDL	58.0
	3	7.3	10.3
	6	7.5± 2.4	14.6± 3.4
Reported sample values are averages based on one to three analyses, see Appendix H for detailed individual results, including values for Ca, Fe, Cu, Zn, and S. QA performed using a Perkin Elmer Optima ICP. QA performed using a Varian 110 ICP. IDL (for Perkin Elmer Optima ICP) for As = 1.4 ppb; P = 2 ppb; and Ca = 2.9 ppb. IDL (for Varian 110 ICP) for As = 44 ppb; P = 17 ppb; and Ca = 250 ppb.			

Table 4-13. Summary of experimental results for long-term air sparging of room temperature precipitated apatite-like products: ASARCO system.

Sample Description		Concentration, µg/L	
		Arsenic	Phosphorus
Starting Water		3.8± 0.9 g/L ¹	10.1± 1.3 g/L ¹
Nominal P/As mole ratio in the initial solution	Months		
0	0	2775.7	66.5
	3	218,400± 4,800	143± 19
	6	601,040± 58,900	
5	0	27.6	50.3
	3	13.8± 6.2, see note	41.6± 1.4
	6	10.6± 0.8	8.9± 1.1
7	0	23.9	36.6
	3	10.2± 10.6 see note	42.1± 1.4
	6	28.9± 0.6	13.0± 1.9

Table 4-13. Summary of experimental results for long-term air sparging of room temperature precipitated apatite-like products: ASARCO system.

Sample Description	Concentration, µg/L	
	Arsenic	Phosphorus
Reported sample values are averages based on one to three analyses, see Appendix H for detailed individual results, including values for Ca, Fe, Cu, Zn, and S.		
P/As = 5 at 3 months: one data point rejected, see Appendix H.		
P/As = 7 at 3 months: one data point was < IDL. Average based on using 1.4 ppb for that value.		
QA performed using a Perkin Elmer Optima ICP.		
QA performed using a Varian 110 ICP.		
IDL (for Perkin Elmer Optima ICP) for As = 1.4 ppb; P = 2 ppb; and Ca = 2.9 ppb.		
IDL (for Varian 110 ICP) for As = 44 ppb; P = 17 ppb; and Ca = 250 ppb.		

Table 4.14. Elemental concentrations in solids aged for 6 months in air sparged slurry samples.

Sample	Description	Elemental Concentration, %		
		As	Ca	P
APHAP-221497P/As7	Synthetic Solution Precipitated Solids: P/As = 7	2.92± 0.05	46.3± 1.3	8.9± 0.1
BERK-3597P/As7	Berkeley Pit Water Precipitated Solids: P/As = 7	0.45± 0.04	30.1± 0.6	1.13± 0.03
ASARCO-3597P/As7	ASARCO Blow-down Water Precipitated Solids: P/As = 7	5.25± 0.11	41.0± 2.1	9.78± 0.20
All elemental concentration determinations are based on triplicate digestions.				
P/As: nominal mole ratio of 7 in the initial solution prior to precipitation.				
Instrument Detection Limits for Perkin Elmer Optima ICP: for As = 1.4 ppb; P = 2 ppb; and Ca = 2.9 ppb.				

Table 4-15. Particle size distribution for room temperature precipitated solids (P/As = 7, Ca/(As+ P) = 3.7).

Size, nanometers	Distribution by response, %		
	Intensity	Volume	Number
52.7	0.0	0.0	0.0
66.4	0.0	0.5	7.9
83.6	1.0	2.1	23.1
105.3	3.7	3.7	26.8
132.5	7.8	4.4	17.8
166.9	12.2	4.3	9.0
210.7	15.7	3.9	4.2
264.5	17.2	4.5	2.1
333.0	16.2	19.8	3.0
419.3	13.0	33.9	4.0
527.9	8.3	18.6	1.9
664.7	3.8	3.0	0.1

Table 4-15. Particle size distribution for room temperature precipitated solids ($P/As = 7$, $Ca/(As + P) = 3.7$).

Size, nanometers	Distribution by response, %		
	Intensity	Volume	Number
836.9	0.9	1.2	0.0
1053.7	0.0	0.1	0.0
1326.7	0.0	0.0	0.0
Mean	299.7	bimodal 143.7(81.9 half width, hw), 420.6 (222.2 hw)	bimodal 116.4 (77.0 hw), 389.6 (191.3 hw)
Average particle size	299.1	376.4	143.2

Table 4-16. Specific gravity of newly precipitated and 6-month air-exposed aged APHAP, Berkeley Pit, and ASARCO products.

Solid	Specific gravity, g/cc	
	T = 0	T = 6 months
HAP, reagent (Ref. 34)	3.4	
Pure system, P/As = 0, Ca/(As+ P) = 3.67	3.4	3.3
Pure system, P/As = 5, Ca/(As+ P) = 3.67	3.5	2.7
Pure system, P/As = 7, Ca/(As+ P) = 3.67	2.6	3.0
Berkeley pit system, P/As = 0, Ca/(As+ P+ SO ₄) = 2.5	-	3.0
Berkeley pit system, P/As = 5, Ca/(As+ P+ SO ₄) = 2.5	-	2.9
Berkeley pit system, P/As = 7, Ca/(As+ P+ SO ₄) = 2.5	-	2.5
ASARCO system, P/As = 0, Ca/(As+ P+ SO ₄) = 2.5	2.7	2.4
ASARCO system, P/As = 5, Ca/(As+ P+ SO ₄) = 2.5	2.7	2.8
ASARCO system, P/As = 7, Ca/(As+ P+ SO ₄) = 2.5	2.8	2.5
Specific gravity values are an average of duplicate or triplicate determinations.		

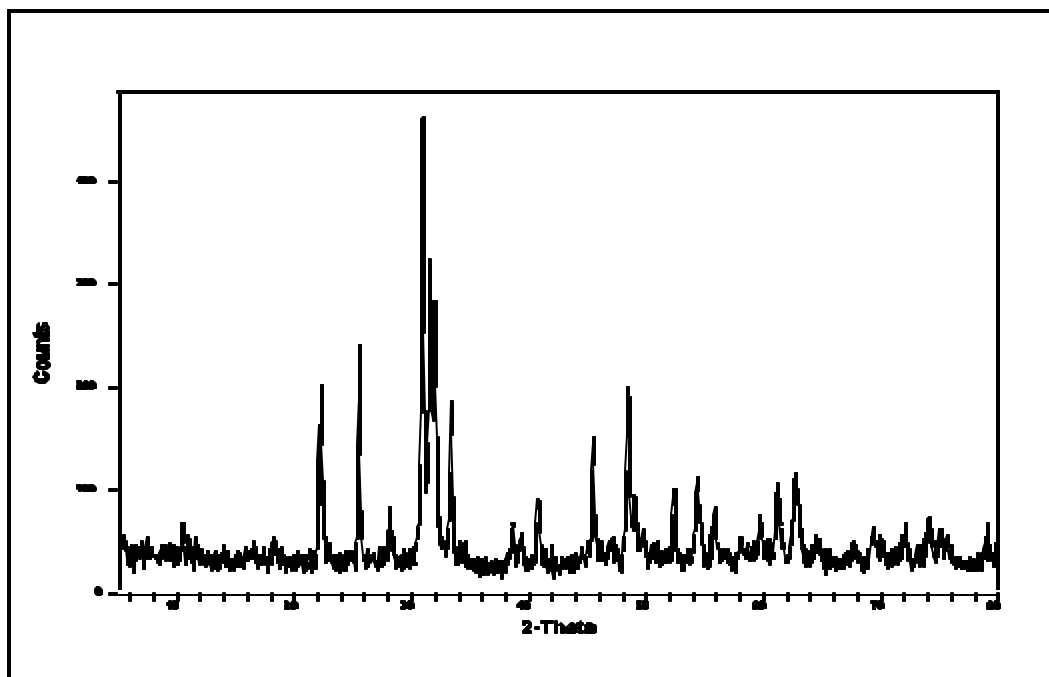


Figure 4-1. XRD pattern for AHAP.

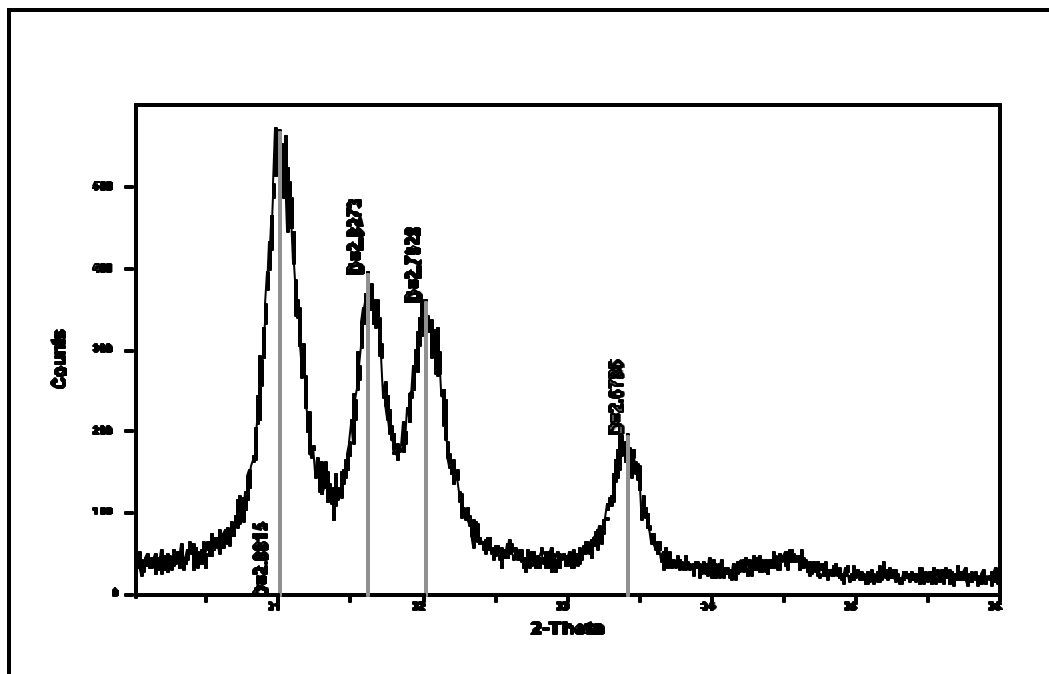


Figure 4-2. XRD pattern for AHAP over the 2-theta range 30–36E.

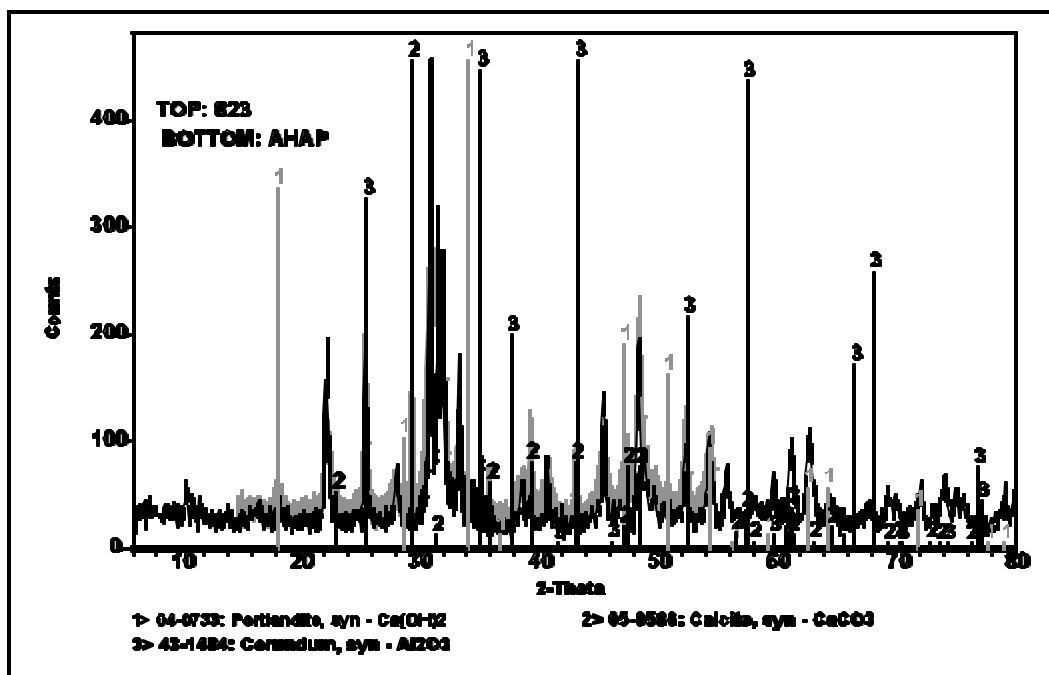


Figure 4-3. XRD pattern for ambient temperature precipitated AHAP aged at ambient temperature for 4 years (top pattern) with the high temperature precipitated sample pattern superimposed (bottom pattern).

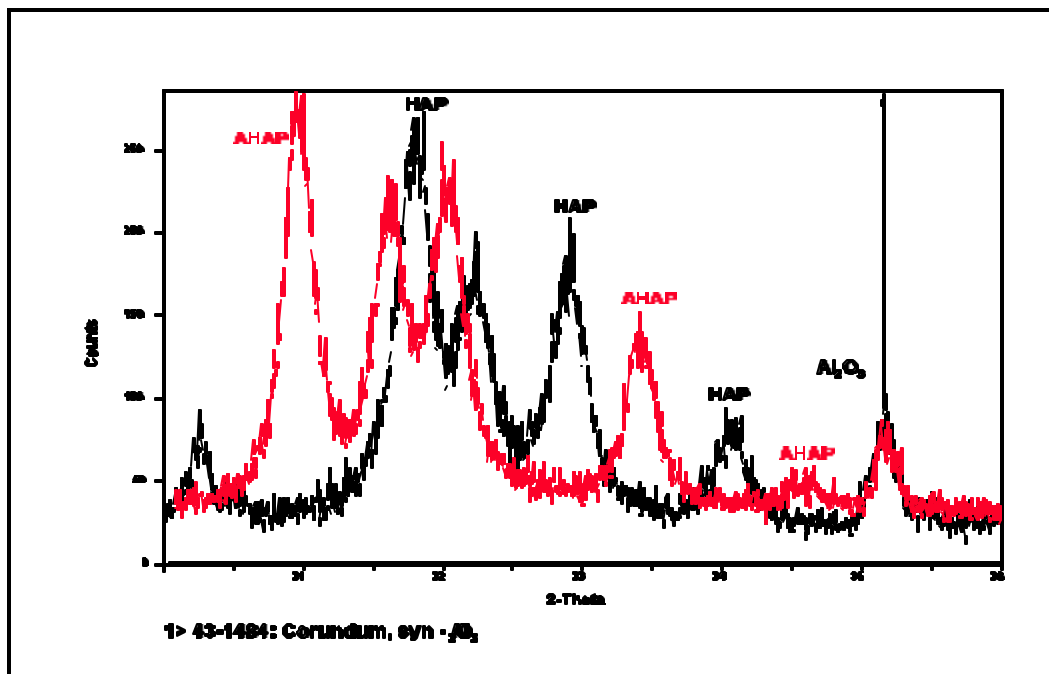


Figure 4-4. XRD patterns for AHAP (no phosphate) and HAP (no arsenate).

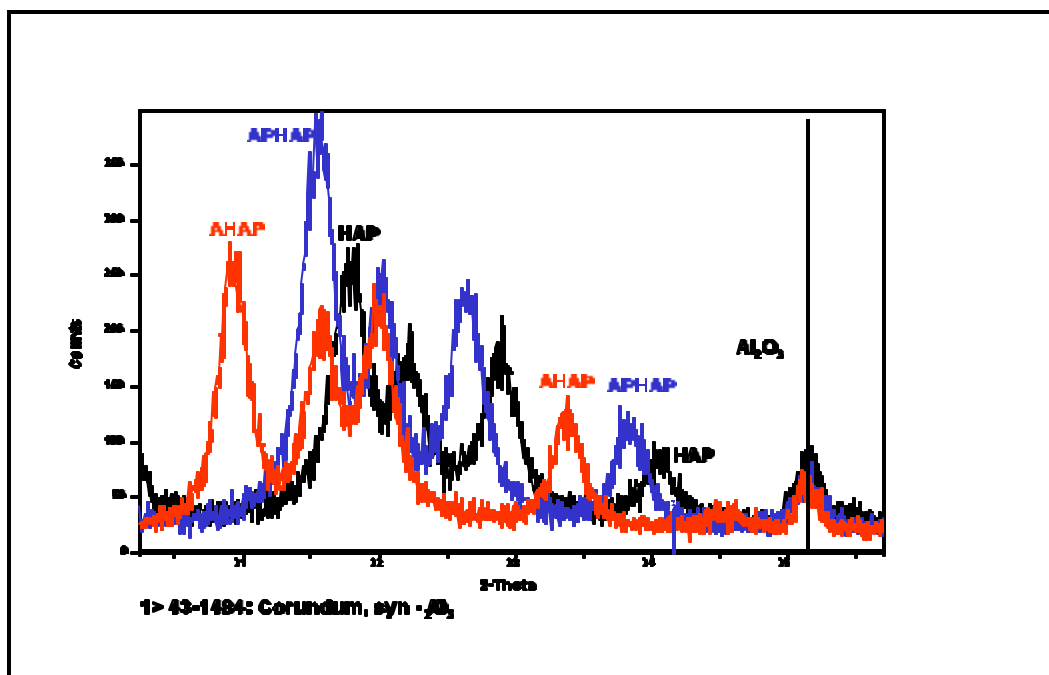


Figure 4-5. XRD patterns for AHAP (no phosphate), APHAP (P/As mole ratio in solids = 1.9), and HAP (no arsenate).

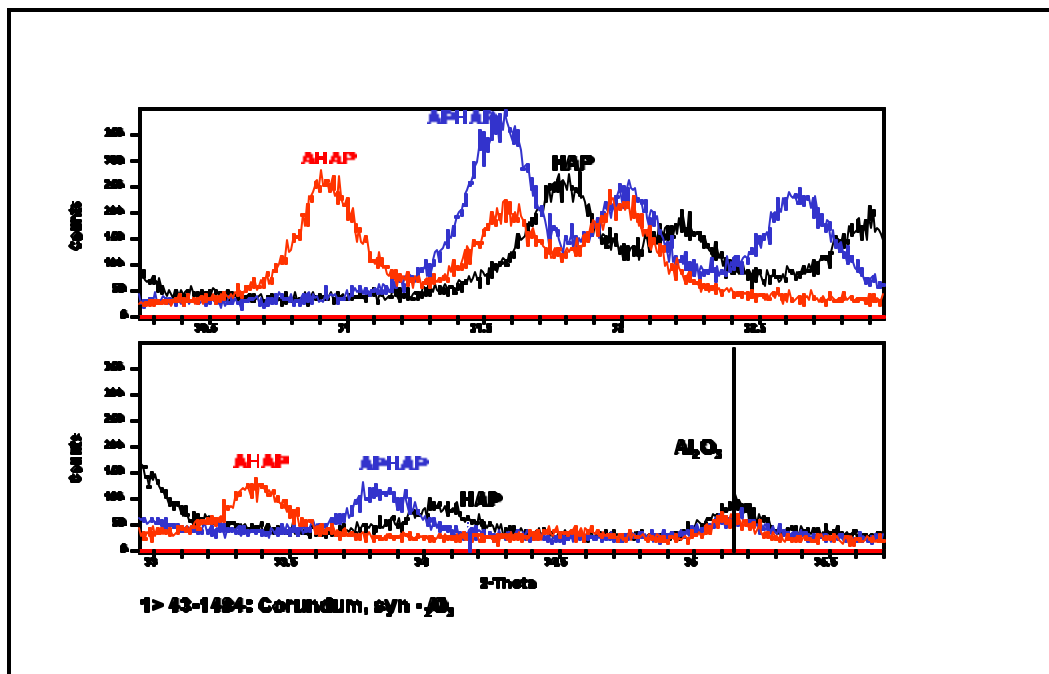


Figure 4-6. XRD patterns for AHAP (no phosphate), APHAP (P/As mole ratio in solids = 1.9), and HAP (no arsenate) (expanded view).

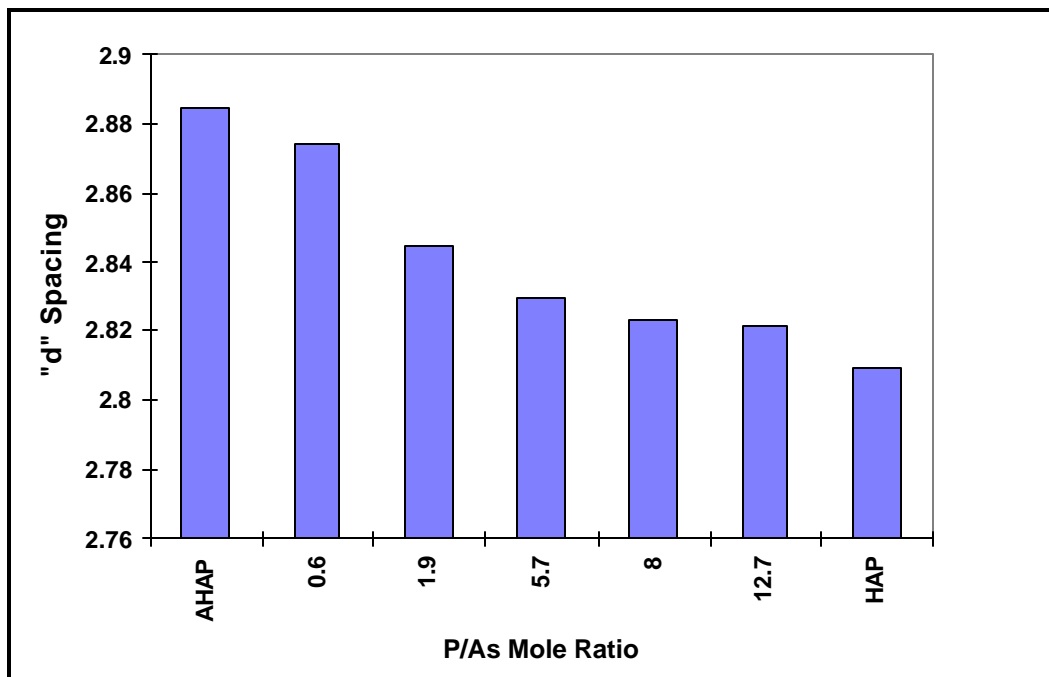


Figure 4-7. Shift in the major peak for apatite-like compounds as a function of the P/As mole ratio in the solid compound.

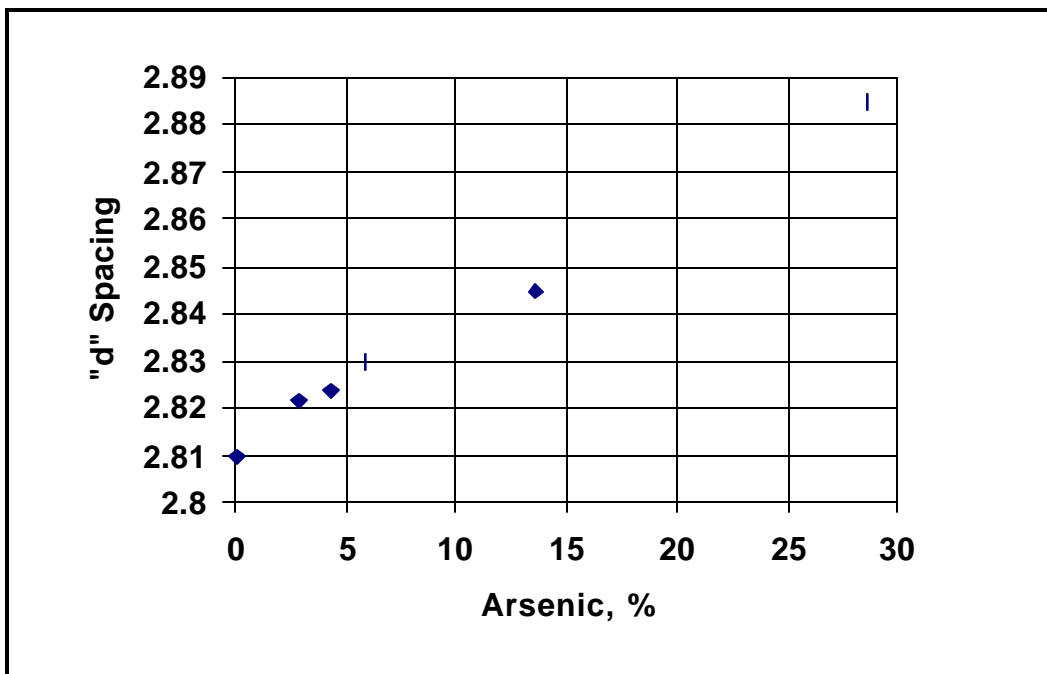


Figure 4-8. Shift in the major peak for apatite-like compounds as a function of the arsenic content in the solid compound.

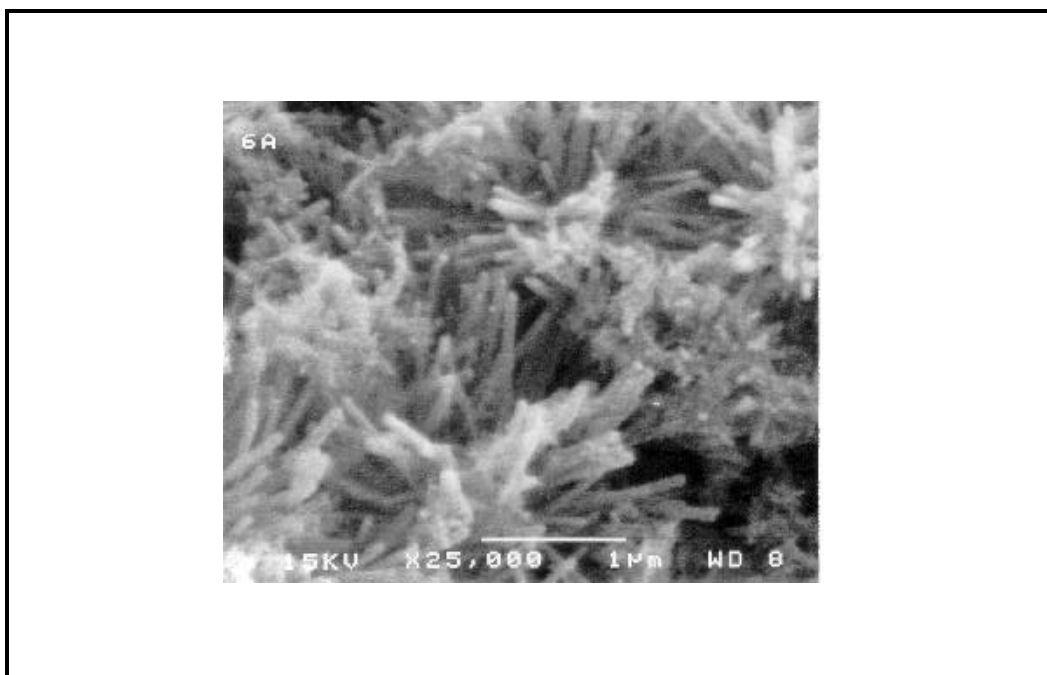


Figure 4-9. AP-HAP photomicrograph (formed from a solution at 95 EC containing a P/As mole ratio of 0.7).

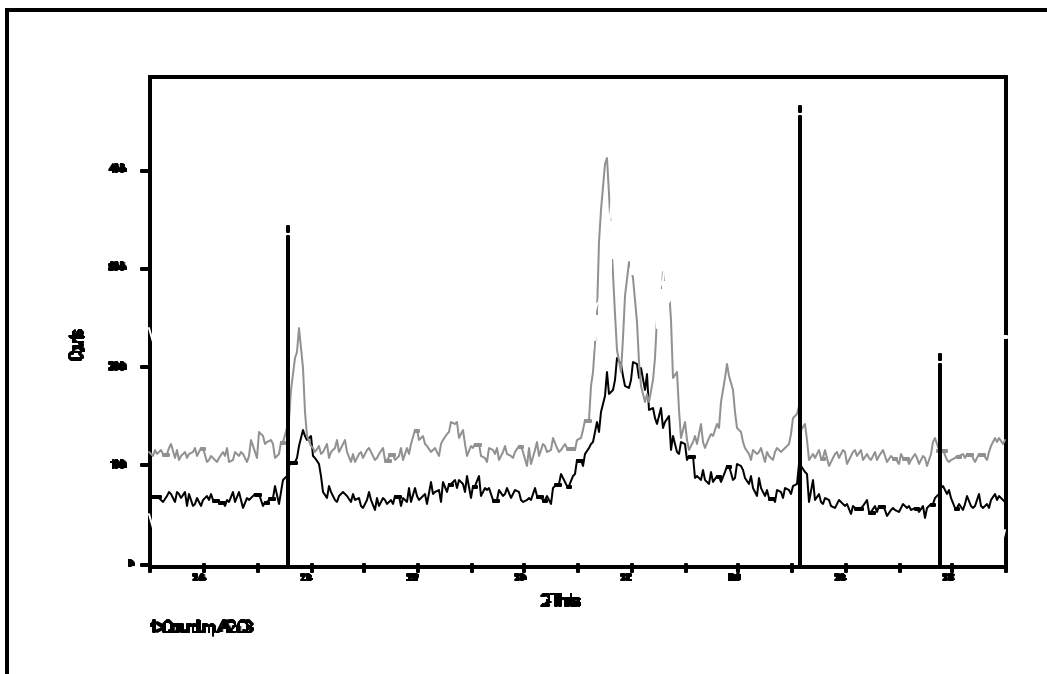


Figure 4-10. Ambient temperature APHAP ($P/As = 7$) aged at 90–95 EC for 5 days. The bottom curve is the pattern for ambient temperature precipitated APHAP. The top dotted curve is the pattern for the ambient temperature solids aged at 95 EC for 5 days.

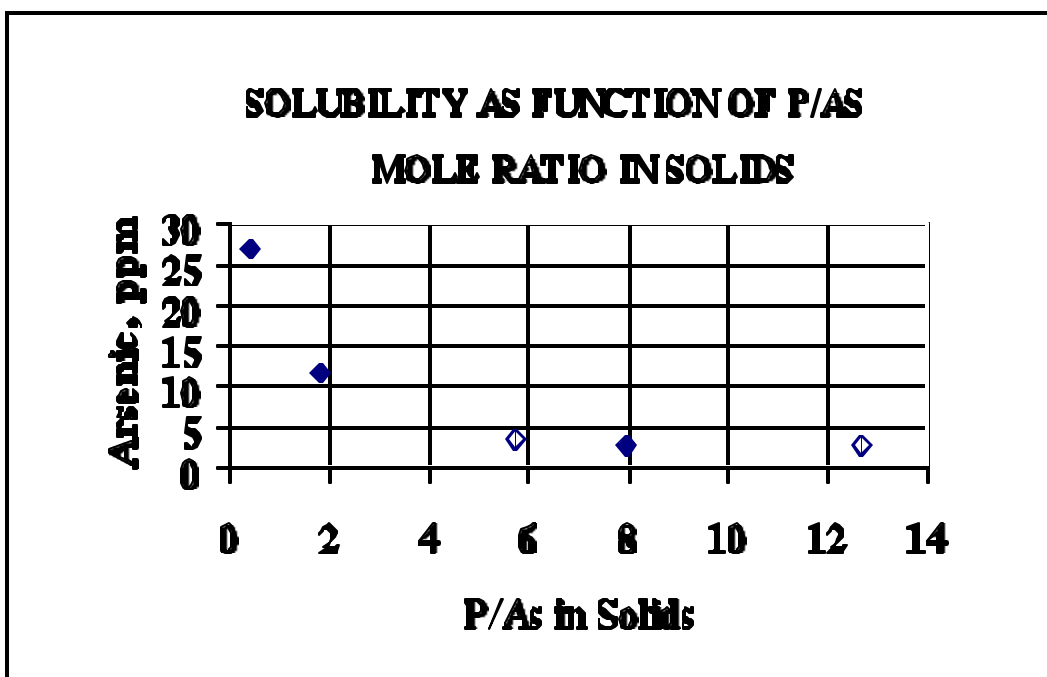


Figure 4-11. Solubility of arsenic as a function of the P/As mole ratio in the apatite-like solids.

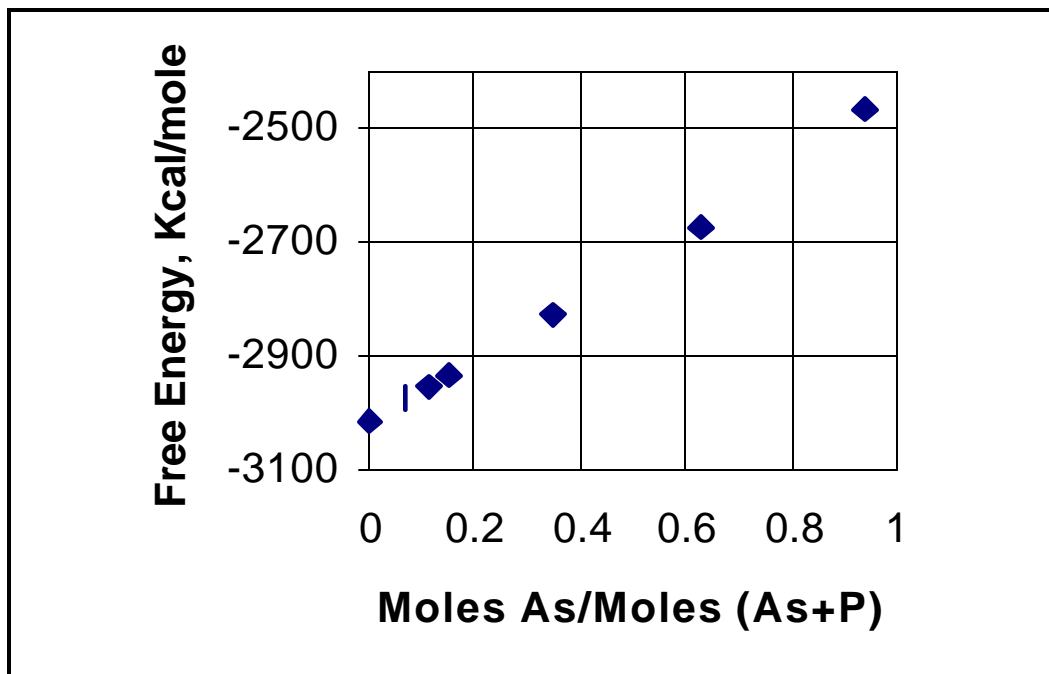


Figure 4-12. Free energy of formation of APHAP as a function of mole fraction of arsenic [with respect to the arsenic/(arsenic + phosphorus) mole ratio].

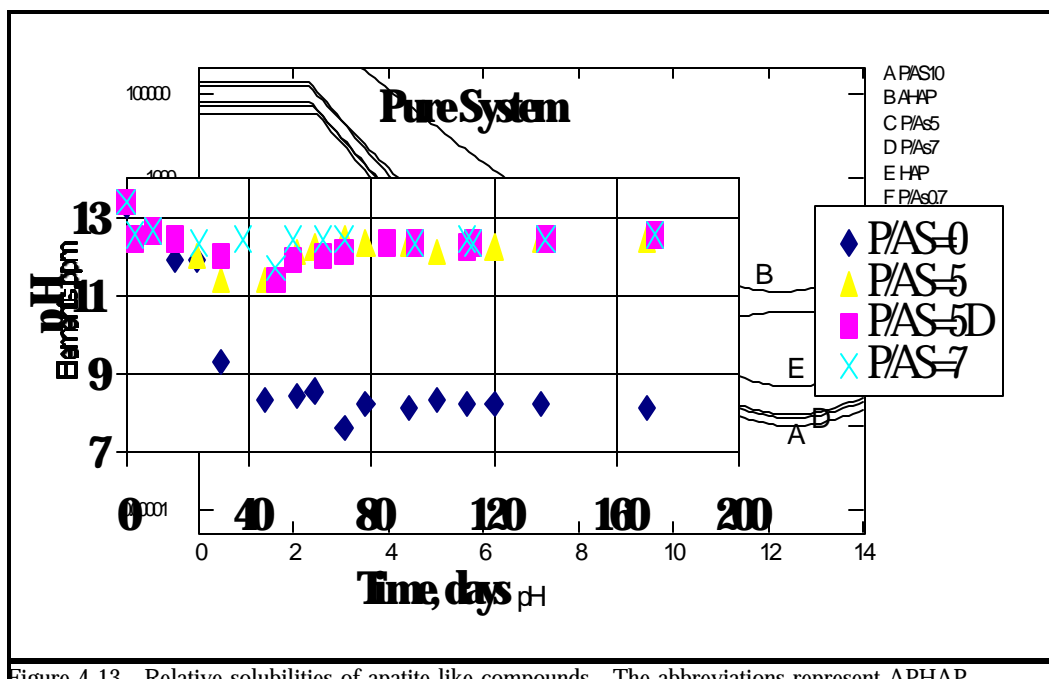


Figure 4-13. Relative solubilities of apatite-like compounds. The abbreviations represent APHAP compounds formed from solutions containing nominal ratios specified, i.e., P/As = 0, 5, 7, 10 and no As (AHAP).

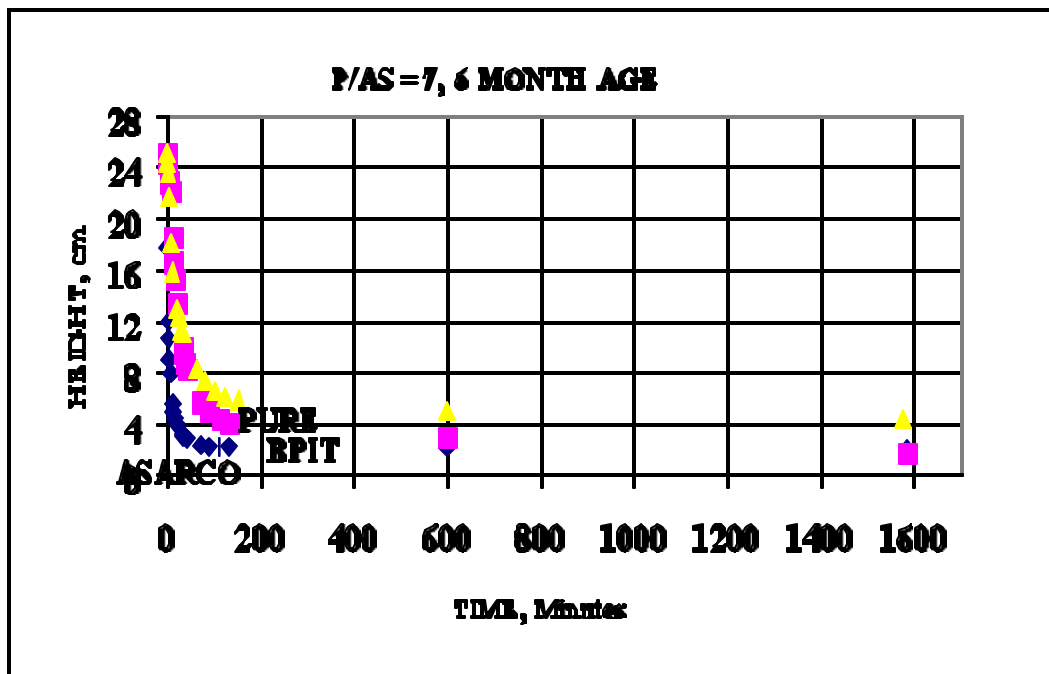


Figure 4-15. Settling rates for 6-month air-aged precipitated products.

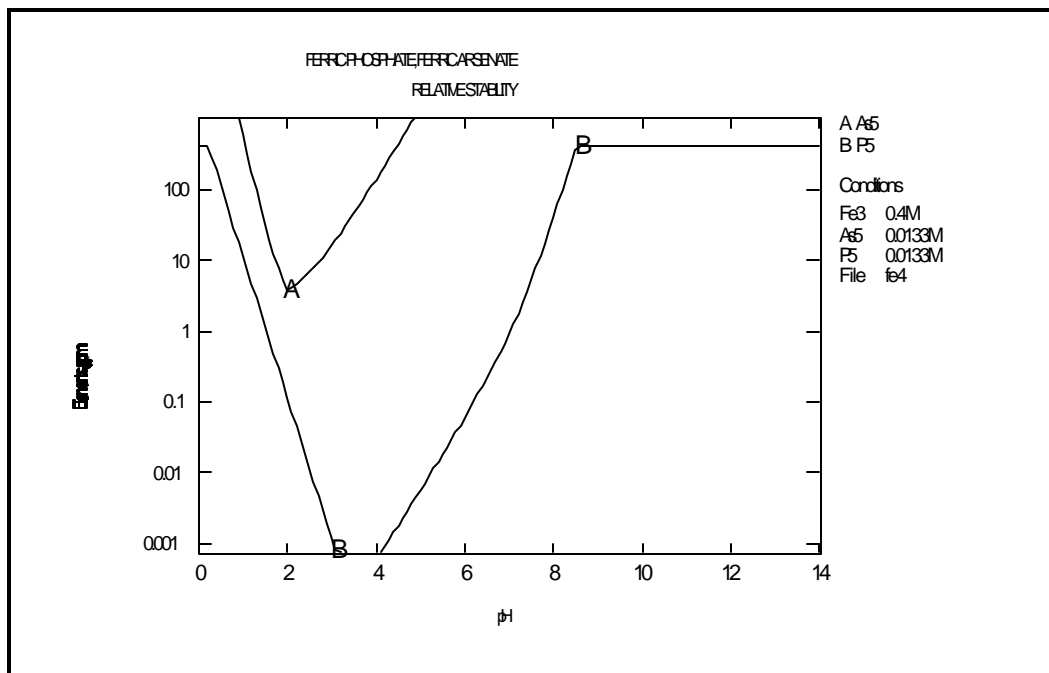


Figure 4-16. Comparison of the relative solubilities for ferric arsenate and ferric phosphate.

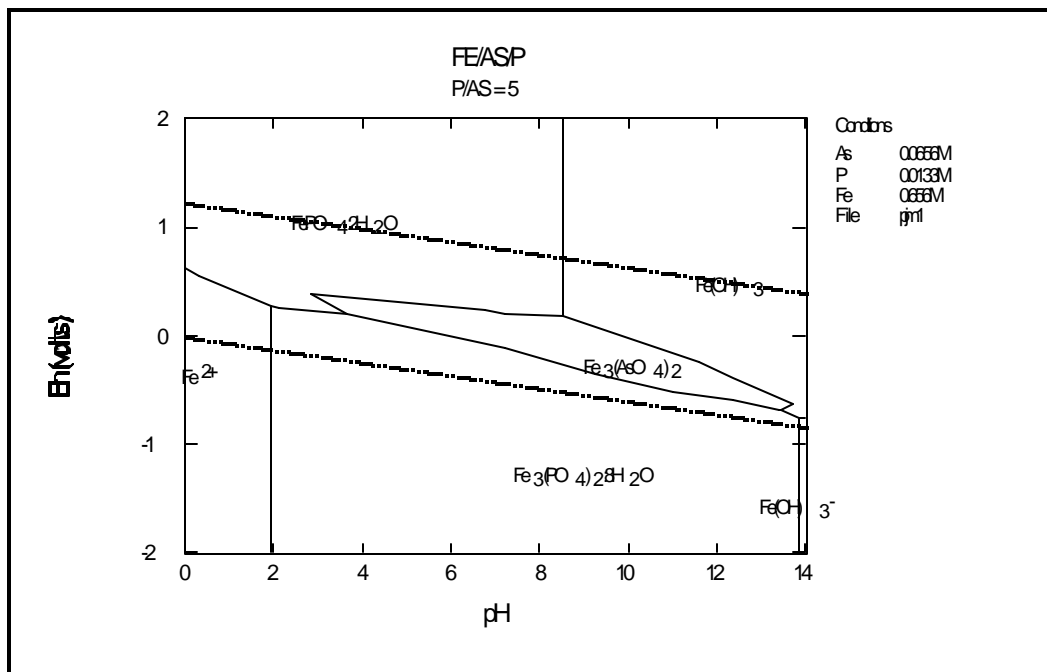


Figure 4-17. E_h /pH diagram for the Fe/As/P water system.

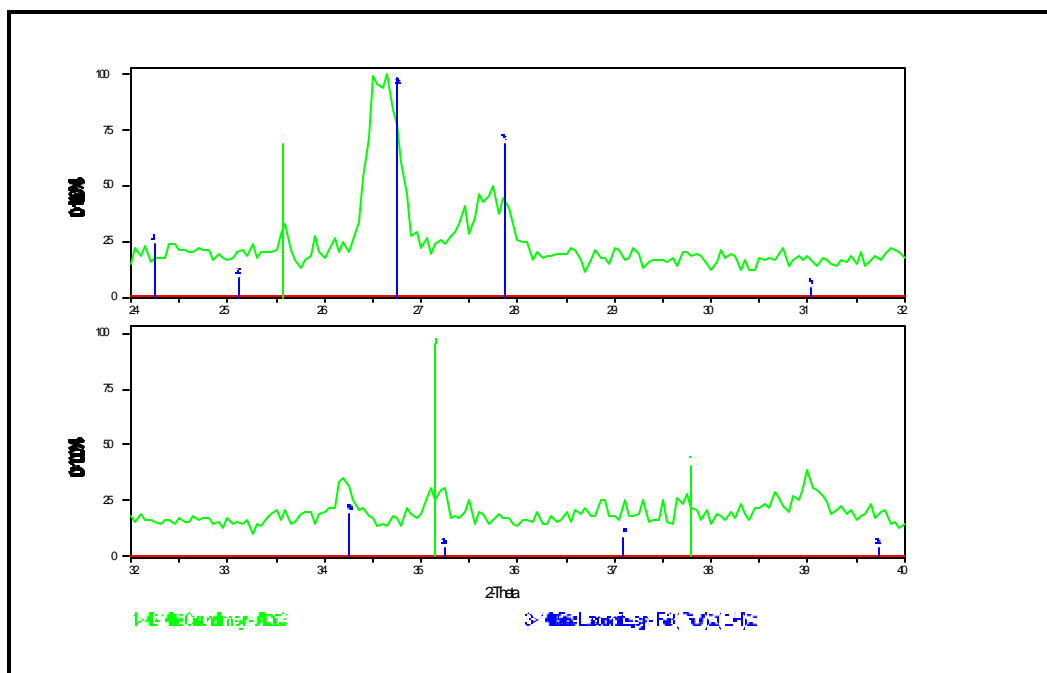


Figure 4-18. XRD pattern for the precipitated product from the Fe(II)/As/P test work at pH 7.8.

5. Economic Analysis

One of the objectives of this study was to perform a first order cost estimation for the developed treatment flow sheet. Therefore, a “first order” cost estimate was performed on the flow sheet presented in Figure 5-1. The cost estimate presented here is not a detailed engineering cost analysis; it is only a first order cost estimate that should be within $\pm 30\%$.

Definitions and cost estimation factors were taken primarily from *Mineral Processing Equipment Cost and Preliminary Capital Cost Estimation* (Ref. 39). Itemized equipment lists were used where possible, and literature quoted cost figures were used where available. All costs were updated to the fourth quarter 1996 using the Marshall and Swift (M&S) Index (Ref. 40). The current (fourth quarter 1996) M&S Index value was 1045.1.

Major cost items were included. The factored capital cost (FCC) totals included minor equipment, instrumentation, processing piping, auxiliary engineering, and plant size factors; an example is presented in Table 5-1. Detailed cost sheets, both for capital and operating costs are presented in Appendix M (Tables M-1 through M-8).

Capital costs and operating cost were estimated. Equipment costs were based on cost equations of the form:

$$\text{Cost}_{\text{now}} = a(\text{capacity})^b (\text{M\&S}_{\text{now}} / \text{M\&S}_{\text{then}})$$

Where, a and b are constants for a particular piece of equipment (taken from Mular, Ref. 39).

FCC and Factored Capital Annual Cost (FCAC)

A flowsheet was developed based on present laboratory studies (Figure 5-1). Mass flow calculations were performed based on two very different waters and different flow rates, e.g., 300 gallons/minute for 365 days per year containing 500 ppb arsenic and 20 gallons/minute for 365 days per year containing 3 gallons per liter (gpl) arsenic. Assumptions made for the cost estimate are presented in Table 5-2.

An equipment list was prepared for each unit of operation, and the cost was estimated as described above. The FCC was determined by using the factors presented in Table 5-1 (selected factors for this study are presented in bold in enlarged font). A FCAC was then determined based on a five-year payoff, 10% interest rate.

Operating Cost

Annual operating cost estimates were established based on reagent consumption, manpower requirements, maintenance, and power consumption. Reagent consumption was based on calculated mass flow. Reagent costs were taken from the Chemical Market Reporter (Ref. 40). Manpower requirements, maintenance, and power consumption were estimated using the following factors, i.e., manpower 20% FCAC, maintenance 5% FCAC, and power 4% FCAC.

Annualized Cost

The total annualized cost are summarized in Table 5-3 and includes reagent mixing, precipitation, thickening and filtering.

Ramalho (Ref. 42) presented estimated treatment cost data for removing impurities (0.5 pounds/1,000 gallons) from wastewaters. His reported value is 45 cents/1,000 gallons (based on 1983 data). This cost has been updated to present utilizing a cost index ratio ($M\&S_{\text{now}}/M\&S_{1983} = 1045.1/800 = 1.31$). The resulting treatment

cost is 59 cents/1,000 gallons. This cost value is for removing impurities from solutions by adsorption and ion exchange technologies. The values do not, however, include treating the impurity laden product solutions that would, in most cases, be appreciable. Even though the cost for the present apatite-like process is higher, the resulting product is a “throw-away” product, i.e., no further treatment is necessary other than storage in a tailings pond environment.

A better comparison of cost (based on a closer fit between the basis assumptions for the cost estimates) for treating acid mine waters is presented by Canonie Environmental (Ref. 43). Their estimate for treating Berkeley Pit water by lime neutralization is \$2–\$4/1,000 gallons (for capital cost only; in 1992 dollars) of water treated (at a rate of 400,000 gallons per day).

A cost comparison for the high arsenic ASARCO blowdown water is not available. Presently, ASARCO at their East Helena, Montana smelter treats their blowdown water by the Tetra Tech HDS (high density sludge) patented process. Their process is a lime precipitation/recycle process (to build up the solids content of the final product). The treatment cost by the HDS process is currently proprietary.

Future Cost

A more realistic cost estimate will be made following the completion of the MWTP-MSE demonstration project to be conducted in July 1997.

Table 5-1. Factored capital cost estimate form.

Item	Cost, \$
1. Purchased equipment costs	
2. Installed equipment costs	
Item 1 multiplied by 1.43	
3. Process piping	
Type plant: Percent of Item 2: Solid 7-10% Solid-Fluid 10 -30% Fluid 30-60%	
4. Instrumentation	
Amount of automatic control: Percent of Item 2:	
None 2-5% Some 5 -10% Extensive 10-15%	
5. Buildings and site development	
Type plant: Percent of Item 2:	
Outdoor 5-20% Outdoor-Indoor 20 -60% Indoor 60-100%	
6. Auxiliaries (e.g., electric power)	
Extent: Percent of Item 2:	
Existing 0% Minor additions 0- 5 % Major additions 5-25% New facilities 25-100%	

Table 5-1. Factored capital cost estimate form (cont'd).

Item	Cost, \$
7. Outside lines	
Average length: Percent of Item 2:	
Short 0–5% Intermediate 5 –15% Long 15–25%	
8. Total physical plant costs: Sum of Items 2+ 3+ 4+ 5+ 6+ 7	
9. Engineering and construction	
Complexity: Percent of Item 8:	
Simple 20 –35% Difficult 35–60%	
10. Contingencies	
Type process: Percent of Item 8:	
Firm 20% Subject to change 20 –30% Speculative 30–50% Average 30%	
11. Size factor	
Size plant: Percent of Item 8:	
Large commercial 0–5 Small commercial 5 –15 Pilot plant 15–35	
12. Factored Capital Costs: Sum of Items 8+ 9+ 10+ 11	
Note: Percentages selected for this study are marked bold in larger font size.	

Table 5-2. Cost estimate assumptions.

Item	Assumptions
Site	Treatment will be conducted at a currently operating facility. Major buildings (containing sufficient space for the treatment process) are available. Analytical capabilities exist. Tailings ponding facilities are in place.
Permitting	Regulatory permits are in place.
Flow characteristics	Treatment system a: 300 gallons/minute, 365 days/year, containing 500 ppb arsenic. Treatment system b: 20 gallons/minute, 365 days/year, containing 1,000,000 ppb arsenic.

Table 5-3. Summary of process cost.

System	FCC, \$	FCAC, \$/yr	Oper. cost, \$/yr	Total cost, \$/yr	Cost, \$/1000 gal	Cost, ¢/gal
300 gallons/minute, 500 ppb As	350,300	90,800	27,600	118,400	0.74± 0.21	0.07± 0.02
20 gallons/minute, 1 g/L As	156,800	40,700	143,700	184,300	17.5± 5.2	1.75± 0.52
For detailed calculations refer to Appendix M, Tables M1–M8.						



Figure 5-1. Flowsheet for treating arsenic bearing solutions by apatite-like compound formation.

6. Quality Assurance/Quality Control

This project was conducted to identify and develop appropriate techniques to remove arsenic from mine waters by producing stable solids that can be safely stored in conventional tailings ponds. The purposes of the project were to evaluate the use of phosphate additions to wastewaters to precipitate apatite-like solids, $\text{Ca}_{10}(\text{As}_x\text{P}_y\text{O}_4)_6(\text{OH})_2$, to effectively strip arsenic from the water, and to demonstrate that the solid products would be stable against conversion to calcium carbonate when stored as a slurry under conventional tailings pond conditions (a high pH environment exposed to air). The programmatic and regulatory setting in which the project quality assurance was conducted was Category III.

The QAPP complied with the requirements of a Category III project plan. Category III projects are those producing results to be used to evaluate and select basic options or to perform feasibility studies or preliminary assessments of unexplored areas. Existing background data use by MWTP participants were not required to conform to either Category II or III criteria.

6.1 Project Objective

The quality assurance/quality control (QA/QC) objectives outlined for the project were specified to generate acceptable data. This QAPP (Ref. 1) provided sufficient details to demonstrate the following:

- C intended measurements were appropriate for achieving project objectives;
- C quality control procedures were sufficient for obtaining data of known and adequate quality; and
- C such data was defensible if challenged technically.

The objective of the project was to identify and develop appropriate techniques to remove arsenic from mine waters by producing stable solids that can be safely stored in conventional tailings ponds. The desired effluent concentration of arsenic was intended to be below the U.S. Drinking Water Standards, i.e., below 50 micrograms of arsenic/liter. The desired solubility concentration for the stored solids was intended to, also, be below 50 micrograms of arsenic/liter.

6.2 Analytical Procedures and Calibration

6.2.1 EPA-Approved Methods

Solutions: Waters and Digested Solutions
Solutions were analyzed at Montana Tech using a Varian Liberty Model 110 Inductively Coupled Plasma Spectrometer (ICP) and a Perkin Elmer Optima ICP using EPA SW 836, Method 6010A (Ref 43). Samples were prepared for ICP analysis according to the procedures outlined in SW 836, Method 3005A. All samples were preserved with nitric acid to form a 5% (v/v) (volume/percent) solution.

Solids

X-ray diffraction analyses were performed using a Phillips 3100 X-ray Generator. X-ray diffraction patterns were generated on samples prepared as outlined in Appendix C. All samples were doped with ten weight percent alumina prior to analysis to ensure that the two-theta spacing value shifts were correct.

X-ray photoelectron spectrometry (XPS) analysis was performed at the Image and Chemical Analysis Laboratory at Montana State University in Bozeman, Montana. ASTM procedures E 1078-90 (Standard Guide for Specimen Handling in Auger Electron

Spectroscopy, X-ray Photoelectron Spectroscopy, and Secondary Ion Mass Spectrometry) were utilized by the Montana State University laboratory.

6.2.2 Equipment Calibration

ICP Calibration

The QA/QC data for ICP analyses were performed throughout this research. The instruments were calibrated according to the procedures outlined in EPA SW 846, Method 6010A and the equipment manufacturer's recommendations. The acid matrix for the ICP calibration standards was matched to the matrix used to prepare the samples. The internal quality control checks for ICP included:

- C instrument calibration;
- C initial and continuing calibration verifications (CCV);
- C initial and continuing calibration blanks;
- C preparation blank;
- C matrix spike;
- C analytical duplicate samples;
- C serial dilution analysis;
- C laboratory control sample (LCS);
- C interelement correction; and
- C instrument detection limit (IDL) determination (determined quarterly).

PH and Oxidation-Reduction Potential Meters

The pH and oxidation/reduction meters calibration followed the manufacturer's recommended procedures (ORION). Two buffer solutions were used for calibration, usually pH 7 and 12.45. Zobell's solution was used to verify that the oxidation/reduction probe was performing correctly, i.e., the Zobell's solution produced a potential reading (using a silver/silver chloride/platinum probe) of 436 millivolts at 20 EC. If the reading of the standard solution fell outside a range of ± 35 millivolts, the probe was cleaned, and the fill solution was replaced. The calibration checks for the pH and oxidation/reduction meters and probes included an initial calibration verification (ICV) and hourly calibration of instrument operation.

X-ray Diffraction

The XRD system was calibrated using a National Institute of Standards and Testing reference material, i.e., SRM 1976, alumina. The calibration verification procedure was performed quarterly.

7. Field Samples

Two field samples were collected for this project, i.e., Berkeley Pit Water and ASARCO Blowdown Water. Approximately 15 gallons of water was used from each source.

7.1 Berkeley Pit Water

The Montana Bureau of Mines and Geology collected Berkeley Pit water samples from a depth of 200 feet on July 18, 1996. Fifteen gallons of water was collected that was used for all bench-scale test work. All water samples were collected from a dedicated vertical sample line and sampling apparatus located on a floating platform in the Berkeley Pit. A 3-inch peristaltic pump was used to withdraw water samples through the vertical sampling line.

Representative samples were collected. Three sample line volumes were pulled through the sampling system and discarded prior to collecting samples for this project. Purge volumes were determined, and the volumes were recorded for the specific samples collected for this project. Samples were transferred directly from the

sample line into 5-gallon HDPE carboys. These samples were refrigerated at 4 EC until they were used for test work. All samples were used unoxidized.

7.2 ASARCO Blowdown Water

MSE Technology Applications personnel collected ASARCO blowdown water on July 25, 1996, from the clarified acid water storage tanks located on the ASARCO Lead Smelting Plant site in East Helena, Montana. Samples were collected from a tap used by ASARCO personnel for sampling purposes. Sample taps were flushed with deionized water prior to collecting the samples for this project. Samples were collected directly from the tap into 5-gallon HDPE carboys. Samples were placed in a cooler and transported immediately to Montana Tech. Fifteen gallons of water was collected that was used for all bench-scale test work. These samples were refrigerated at 4 EC until they were used for test work. Most of the water samples used in this test work were oxidized prior to use (oxidization procedure is presented in Appendix H).

8. Bench-Scale Test Work QA/QC Activities

Two important sets of data were generated, i.e., the data necessary to determine the free energy of formation for the APHAP compounds (solubility data) and the data necessary to ascertain that the compounds formed are stable for long-term storage in tailings pond environments. Both sets of data were generated by exposing solids to a solution phase, then analyzing the solution phase for elemental content. The data quality requirements were the same for each set of data. However, the elemental content requirements were somewhat different, i.e., for the solubility samples, it was required that the concentrations of arsenic, calcium, and phosphorus be accurately known; for the long-term aged samples, it was required that only the concentration of arsenic be accurately known. Therefore, the data validation evaluation was conducted with emphases on these requirements.

ppb, and on the Optima instrument the limit was 2 ppb.

8.1 Solubility Data Validation

Quality assurance objectives are summarized in Table 8-1.

The validation summary report for completeness, accuracy, and precision results is presented in Table 8-2. All quality assurance objectives were satisfied.

Contract Required Detection Limits (CRDL) for arsenic and calcium were 20 and 5000 ppb, respectively. The IDL for the Varian Liberty 110 ICP was 44 ppb for arsenic and 250 ppb for calcium. Since the Varian instrument did not meet the CRDL for arsenic, all samples that analyzed less than 100 ppb arsenic were reanalyzed using a Perkin-Elmer Optima ICP (detection limit for arsenic was 1.4 ppb). There was no CRDL required for phosphorus. The detection limit on the Varian instrument was 17

Solution pH was monitored daily in the solubility test bottles for the first 10 days, then they were monitored weekly for the entire test period, i.e., 90 days. The pH was monitored using an Orion 940 pH meter. All pH measurements were taken in the clear supernatant solution (not in the slurry). The pH varied with time until equilibrium was established. Variations in pH for all samples at the time the sample was extracted are presented in Appendix G. The accuracy of the measurements was ensured by careful calibration and recalibration of the pH probe every ten samples or more often if necessary, e.g., a pH buffer solution (at a pH near the sample pHs) was read as a sample repeatedly during each data collecting episode; if the buffer solution did not read the pH within ± 0.2 units, the probe was recalibrated.

Temperature was controlled in a water bath using a Precision Scientific Reciprocal Shaking Water Bath (Model 25). The temperature was monitored daily in the solubility test bottles for the first 10 days, then they were monitored weekly for the entire test period, i.e., 90 days. The temperature was always $25.5 \text{ EC} \pm 0.25 \text{ EC}$. It was unnecessary to adjust the temperature of the control unit during the entire period of the test work.

8.2 Slurry Aging Data Validation

Quality assurance objectives for the aging test work are summarized in Table 8-3. Aging solution concentration data are summarized in Tables 4-9 through 4-11 and are presented in detail in Appendix H. The experimental procedures used are presented in Appendix H and in the Quality Assurance Project Plan (Ref. 1).

The validation summary report for completeness, accuracy, and precision results is presented in

Temperature was not controlled. All precipitations and subsequent aging were

Table 8-4. All three quality assurance objectives (Table 8.3) were satisfied. The accuracy of the arsenic analyses (based on recovery from spiked samples, i.e., seventeen data points, one point was rejected, see Appendix N) fell within the required range of $\pm 25\%$, e.g., the actual variation was within -6% to $+16\%$. The accuracy of the calcium analyses (based on recovery from spiked samples, i.e., ten data points, one point was rejected, see Appendix N) fell within the required range of $\pm 25\%$, e.g., the actual variation was within -11% to $+17\%$. Accuracy for phosphorus analyses could not be determined by sample spiking because all the samples contained sufficient calcium so when they were spiked with phosphorus a precipitate formed; therefore, accuracy was determined by repeatedly analyzing a known phosphorus standard throughout the analytical test work. The accuracy for the phosphorus analyses was well within the ± 25 objective, i.e., the actual variation for thirteen data points was within -17% to $+6\%$.

Solution pH (a noncritical measurement) was monitored weekly in the aging bottles throughout the 6-month test period. The pH was monitored using an Orion 940 pH meter. Representative plots of pH versus time are presented in Appendix H. The accuracy of the measurements was ensured by careful calibration and recalibration of the pH probe every ten samples or more often if necessary, e.g., a pH buffer solution (at a pH near the sample pHs) was read as a sample repeatedly during each data collecting episode; if the buffer solution did not read the pH within ± 0.2 units, the probe was recalibrated.

conducted at ambient temperature. The temperature is estimated between $20\text{--}28 \text{ EC}$.

8.3 Outside Laboratory Analyses

The QA manager sent five samples to an outside laboratory for analyses as a check on the quality of the data generated during this investigation.

The results of the outside analyses and a comparison with project data are presented in Table 8-5.

The project goal for this study for arsenic concentration measurements (Ref. 1) was $\pm 25\%$. The accuracy of the Montana Tech arsenic analyses (only arsenic was a critical measurement in the long-term study) as reported above for the long-term aging study fell within the required range of $\pm 25\%$, e.g., the actual variation was within -5.6% to $+16.4\%$. The accuracy of the Montana Tech arsenic, calcium, and phosphorus analyses (all three element concentrations were critical measurements in the solubility study), as reported above, fell within the required range of $\pm 25\%$, e.g., the actual variation was within

-13.2% to $+0.5\%$ for arsenic; within -17.5% to $+7.9\%$ for calcium; and within -10.1% to $+0.5\%$ for phosphorus. Practically all of the data collected during this study is based on triplicate analyses and QA ICP protocol (except where noted). Therefore, even though the project data for the low arsenic concentration did not agree with the ACZ results to within $\pm 25\%$, all project data (except for the flagged and rejected data points) are deemed valid.

Table 8-1. Quality assurance objectives for solubility test work.

Parameter	Accuracy ¹	Completeness ³	Precision ^{4,5}
Dissolved Arsenic	± 25%	80%	#20% RPD
Dissolved Phosphorus	± 25% ²	80%	#20% RPD
Dissolved Calcium	± 25%	80%	#20% RPD
pH	± 0.2	80%	± 0.2
Temperature	25.5 ± 0.25	80%	NA
1 Accuracy = (measured concentration in ICV, LCS, CCV, 10 ppm standard/known concentration)*100. Concentrations for arsenic, calcium in ppm: ICV = 1,500; LCS = 0.5, 250; CCV = 0.5, 250; 10 ppm std. = 10, 10. 2 Accuracy = (measured concentration in 10 ppm standard/known concentration)*100. 3 Completeness = (samples judged valid/no. samples)*100. 4 Precision (RPD) = (different in dupl. concentrations/average of dupl. concentrations)*100. 5 Precision for solubility analyses (RPD) = (standard deviation/mean of analyses)*100. pH measured but uncontrolled in test system. Temperature controlled.			

Table 8-2. Quality assurance summary for solubility test work.

ICP Event Date	Description of majority of samples	Completeness ¹ , %				Accuracy, % ² /No. samples			Precision, RPD ⁴ , %/No. samples		
		No. Samples	As	Ca	P	As	Ca	P ³	As	Ca	P
June 17, 1996	Solubilities	16	87.5	87.5	100.0	86.8-109.3/5	89.4-101.1/5	95.0-95.1/2	0.0-2.3/7	0.4-5.6/7	0.1-12.8/11
June 18, 1996	Digestions of solids used in solubility tests	16	100.0	100.0	100.0	97.7-108.4/5	82.5-102/5	95.0-95.1/2			
September 17, 1996	Solubilities	27	100.0	100.0	100.0	95.7-107.6/9	92.3-107.1/9	89.9-96.4/3			
November 9, 1996	Solubilities	9	100.0	100.0	100.0	195.0-110.3/6	98.3-105.7/6	95.6-100.5/2			
1 Completeness = (samples judged valid/no. samples)*100.											
2 Accuracy = (measured concentration in ICV, LCS, CCV, 10 ppm standard/known concentration)*100. Concentrations for arsenic, calcium in ppm: ICV = 1,500; LCS = 0.5, 250; CCV = 0.5, 250; 10 ppm std. = 10, 10.											
3 Accuracy = (measured concentration in 10 ppm standard/known concentration)*100											
4 Precision (RPD) = (different in dupl. concentrations/average of dupl. concentration)*100											

Table 8-2. Quality assurance summary for solubility test work (cont'd).

ICP Event Date	Description of majority of samples	Precision for solubility, RPD, % ¹ /No. samples		
		As	Ca	P
June 17, 1996	Solubilities	0.04–2.9/11 ²	0.08–7.4/13	0.3–2.7/6
June 18, 1996	Digestions of solids used in solubility tests	0.1–1.6/14	0.1–1.2/14	0.2–1.3/6
September 17, 1996	Solubilities	0.1–2.3/24	0.1–3.9/24	0.0–4.1/12
November 9, 1996	Solubilities and long-term aging	0.0–0.2/6	0.9–23.7/6 ³	0.4–1.4/2
1 Precision (RPD) = (standard deviation/mean of analyses)*100. Must be #20%				
2 One data set rejected, i.e., RPD = 21.8%.				
3 The 23.7 value was for long-term aging samples; the RPD for the solubilities was 0.9–1.1% for four samples.				

Table 8-3. Quality assurance objectives for long-term storage test work.

Parameter	Accuracy ¹	Completeness ²	Precision ³
Dissolved Arsenic	± 25%	80%	#20% RPD
Dissolved Phosphorus	Unspecified	Unspecified	Unspecified
Dissolved Calcium	Unspecified	Unspecified	Unspecified
1 Accuracy = (sample concentration/concentration in LCS)*100			
2 Completeness = (samples judged valid/no. samples)*100			
3 Precision (RPD) = (different in dupl. concentrations/average of dupl. concentrations)*100 pH measured but uncontrolled in test system.			
Temperature was laboratory ambient conditions: uncontrolled.			

Table 8-4. Quality assurance summary for long-term storage test work.

ICP Event Date	Description of majority of samples	Completeness ¹ , %				Accuracy ² , %/No. Samples			Precision, RPD ⁴ , %		
		No. Samples	As	Ca	P	As	Ca	P ³	As	Ca	P
Nov. 15, 18, 1996	Aged solutions for Berkeley Pit and Pure systems	19	100.0	100.0	100.0	94.9–102.2/2	89–111.5/3	93–103.4/4	0.2–4.9 ⁶	0.3–21.2 ⁷	0.4–15.8 ⁸
Dec. 30, 1996	Aged solutions for ASARCO system	17	94.1	100.0	94.1	99.7–111.7/3	114.4–141.4/2	100/1			
Dec. 31, 1996 ⁵	Aged solutions for ASARCO and Pure systems	27	-	100.0	92.6	113.6/1	117.4/1	95.2–99.7/2			
Feb. 28, 1997	Aged solutions for Berkeley Pit, ASARCO, and Pure systems	32	96.9	100.0	96.9	94.6–116.2/3	98.3/1	96.1–103.9/2			
March 4, 1997	Digestions of aged solids for Berkeley Pit, ASARCO, and Pure systems	21	100.0	100.0	100.0	99.6–101.7/2	96.3–97/2	97.6–102.4/2			
March 31, 1997	Digestions of aged solids for Berkeley Pit, ASARCO, and Pure systems	43	100.0	100.0	100.0	94.4–116.4/4	107–101.3/2	93.3–106.7/2			
<div>1 Completeness = (samples judged valid/no. samples)*100</div> <div>2 Accuracy = [(concentration in spiked sample-concentration of spike)/concentration of spike]*100</div> <div>3 Accuracy = (concentration measured in standard/concentration in standard)*100</div> <div>4 Precision (RPD) = (different in duplicate concentrations/average of duplicate concentration)*100</div> <div>5 All samples rejected for arsenic.</div> <div>6 Thirteen duplicate analyses, two samples rejected (see Appendix N).</div> <div>7 Twelve duplicate analyses, no samples rejected (see Appendix N).</div> <div>8 Twelve analyses, two samples rejected (see Appendix N).</div>											

Table 8-5. Comparison of project data with ACZ laboratory data.

Project Sample ID	ACZ Sample ID	Description	Concentration, ppb () ¹			
			Arsenic ²		Calcium	
			Project	ACZ ³	Project	ACZ
1	L12973-01	Pure, P/As 7, T 0 M, digestion solution	168900 ± 3800 (17%)	140000	2372000 ± 6400 (13%)	2070000
2	L12973-02	Duplicate of 1	168900 ± 3800 (14%)	145000	2372000 ± 6400 (10%)	2130000
3	L12973-03	Pure, P/As 7, T 6 M, solubility solution	3.4 ± 1.0 (194%)	17	832380 ± 11,200 (11%)	926000
4	L12973-04	Bpit, P/As 7, T 6 M, solubility solution	10.8 ± 7.6 (48%)	23	659000 ± 11000 (2%)	648000
5	L12973-05	Asarco, P/As 7, T 6 M, solubility solution	28.9 ± 0.6 (1398%)	440	312800 ± 2200 (72%)	539000
6	L12973-06	5% HNO ₃ Blank		7		0.2
<p>1 Percent deviation of ACZ values from the average of the Montana Tech values. All Montana Tech values were performed in triplicate. The average is shown ± the maximum variation.</p> <p>2 Arsenic is the only critical measurement for all the aged samples. Calcium is a noncritical measurement.</p> <p>3 The blank concentration for arsenic was subtracted from the reported value prior to calculating the percent deviation.</p>						

9. Conclusions

9.1 Apatite-Like Mineral Formation and Stability

Removal of arsenic from wastewaters has been successfully practiced for many years, i.e., technologies have been available to lower the arsenic concentration of wastewaters to below the U.S. Drinking Water Standards (< 50 ppb). However, one of the major technologies, i.e., lime neutralization, produces sludges that cannot be safely stored in outdoor tailings ponds. These sludges release the arsenic back into the solution phase as the calcium arsenate compounds convert to calcium carbonate (by reaction with carbon dioxide in air). The other major industrial technology, i.e., ferrihydrite precipitation with concurrent adsorption of arsenic onto the ferrihydrite surface, produces sludges that may not be stable under long-term storage conditions because the amorphous ferrihydrite is not a thermodynamically stable phase. The thermodynamically stable phase is hematite or goethite, so eventually the meta-stable ferrihydrite will convert to a more stable equilibrium phase. When this conversion occurs, the surface area of the initial ferrihydrite will be greatly decreased; and when the surface area decrease occurs, arsenic is likely to be desorbed from the solid surface back into the solution phase.

The present study has solved the stability problem suffered by the above mentioned technologies, i.e., compounds are formed that are stable against conversion to calcium carbonate; and since the arsenic sequestration is via compound formation (rather than an adsorption phenomena), the solids are not dependent upon maintaining a certain surface area.

This study has demonstrated that apatite-like compounds, $\text{Ca}_{10}(\text{As}_x\text{P}_y\text{O}_4)_6(\text{OH})_2$, are formed via a simple precipitation process, i.e.,

phosphate is added to the arsenic bearing solution in prescribed amounts to facilitate the formation of arsenatephosphateapatite compounds. These compounds have an exceedingly low solubility under tailings pond pH conditions, and they are more stable than calcium carbonate so that long-term safe storage is ensured.

Recipe

A “recipe” for effective arsenic removal from solution and subsequent stability in tailings pond environments has been formulated. The “recipe” requirements are presented below:

- C Arsenic must be in the arsenate rather than arsenite form;
- C Phosphate is required for a stable, storable solid product to be formed. The P/As mole ratio in the initial solution phase must be equal to or greater than 5;
- C The $\text{Ca}/(\text{As} + \text{P})$ mole ratio in the initial solution phase must be greater than 1.5 times the stoichiometric requirement for formation of the apatite-like compound and the formation of calcium sulfate (if the water contains sulfate).

Project Results

The present project has resulted in the following positive results:

- C Arsenate can be stripped from aqueous solutions, but phosphate enhanced the effectiveness of the precipitation, i.e., the effectiveness is enhanced by controlling the P/As mole ratio in the initial solution phase (see Table 9-1).
- C A series of arsenate bearing hydroxyapatite solid solutions can be formed by controlling the

P/As mole ratio in the initial solution prior to precipitation (see Table 9-2). Laboratory studies have shown that solid solutions containing arsenic concentrations from a few percent to approximately 30% are readily formed. These are new compounds that have never been reported previously. The new compounds stoichiometry have been identified by chemical digestions and their structures by XRD and XPS spectrometry.

- C The free energy of formation of the APHAP compounds were determined (see Table 9-3). This now allows modeling of the stability of the compounds under various solution conditions. One of the important considerations is whether the compounds will be stable to long-term storage in tailings pond environments, i.e., exposure to air. Previously, Dr. R. G. Robins (1985) demonstrated that calcium arsenate compounds are unstable in air because the carbon dioxide in air reacts with the calcium arsenate to form calcium carbonate (with the release of arsenic back to the solution phase). Modeling (using the free energy of formation data collected in this study) of tailings pond conditions shows that compound stability is a function of P/As mole ratio, e.g., compounds with a P/As mole ratio of zero to greater than five should be stable to air exposure in tailings-pond-type storage conditions.
- C The long-term stability of the apatite-like compounds is presently being assessed, i.e., compound stability is being tested by sparging air into aqueous/compound slurries for extended periods of time (data for 6-month stability has been collected; the test monitoring will continue for another 1½ years). The pH, E_H , and solution arsenic, phosphorus, and calcium concentrations are being monitored as a function of aging time. The 6-month data show that the arsenic (no phosphate present) bearing solids slurries are not stable to air exposure (see Table 9-4). The

arsenic/phosphorus bearing solids are all stable to 6-month air exposure, i.e., all samples for all waters under testing (pure system, Berkeley Pit system, and the ASARCO system) show an arsenic solubility of less than 50 ppb.

The conclusions drawn from the long-term aging data are summarized below:

Pure Synthetic System

The AHAP compound (no phosphate present) is not stable, i.e., arsenic is initially removed from the solution (to 57.7 ppb) but is subsequently released back to the solution with aging time to rather high concentrations (e.g., at 6 months the arsenic concentration was 85,100 ppb).

The APHAP compounds (phosphate present in the solid) show very low solubilities at all times. For the P/As = 5 and 7 test systems, the arsenic solubility was < 50 ppb for all times investigated. The goal of this project was to strip and maintain the arsenic concentration at < 50 ppb (less than the current U.S. drinking water standard).

The arsenic solubility for the solids produced by precipitating from a P/As = 7 solution is < 10 ppb. Ten ppb is the current drinking water standard in Japan and Germany.

Berkeley Pit Water

All analyses show that the arsenic concentration is < 50 ppb for all test conditions. There does appear to be a trend of increasing arsenic release with aging time for all the P/As = 0 samples.

The phosphate bearing solids do not appear to be changing with aging time. These tests need to be continued for longer times to ensure that true stability does exist.

ASARCO

The phosphate free test samples are definitely not stable to air sparging over time. Arsenic is

initially removed from the solution (to 2800 ppb) but is subsequently released back to the solution with aging time to rather high concentrations (e.g., at 6-months the arsenic concentration was 601,000 ppb).

The phosphate bearing solid samples show excellent stability with time. All sample solubilities were < 50 ppb.

C A first order economic analysis suggests that the cost of applying the apatite-like precipitation process to low arsenic bearing mine waters is reasonable, e.g., the cost has been estimated to be approximately 74 ± 21 cents/1000 gallons. The estimated cost for treating a very high arsenic bearing wastewater like the ASARCO blowdown water is considerably higher, e.g., the cost has been estimated to be approximately 1.8 ± 0.5 cents/gallon. These costs are competitive with other lime neutralization processes (see Table 9-5).

9.2 Iron/Arsenate/Phosphorus System

The potential for formation of iron/arsenate/phosphate compounds appears to be interesting and possible. Only preliminary exploratory test work has been conducted to date. The results are encouraging but, at least, at this time the concept of forming ferricarsenatephosphate compounds has not been convincingly proven. Further test work is planned, e.g., Twidwell has been funded to further investigate this system (Ref. 38). The

potential advantages of the iron/arsenate/phosphate system over the apatite-like mineral formation system are important:

- C The possibility exists for compound formation under near neutral pH conditions. Therefore, the cost of neutralization should be less. Also, there would be no need to readjust the solution pH before discharge (whereas discharge waters from the apatite-like system will have to be neutralized before discharge).
- C Many mine wastewaters have appreciably iron content. Therefore, iron is a problem element that must almost always be dealt with. In this system, it would be one of the required reagent species.

9.3 Future Demonstrations

MSE (Ref. 41) will be evaluating the apatite-like process this summer (1997) at two separate sites, i.e., an acid mine drainage site in Montana (yet to be selected) and the ASARCO smelter site in East Helena, Montana. The evaluation will be conducted on a high arsenic (1–3 grams per liter), low-flow system (the smelter site) and a low arsenic (400–500 ppb), high-flow system (acid mine drainage site).

Table 9-1. Effectiveness of arsenic removal by phosphate.

System (initial arsenate concentration)	Arsenic after treatment, Fg/L		
	P/As = 0	P/As = 5	P/As = 7
Pure (initial As was 1,000,000 Fg/L)	58	< IDL	-

Berkeley Pit Water (initial As was 100,000 Fg/L)	14	14	< IDL
ASARCO Water (initial As was > 3,000,000 Fg/L)	2776	19	24
The Ca/(As+ P) mole ratio for the pure system was 3.7. The Ca/(As+ P) mole ratios for the Berkeley Pit and ASARCO systems were 2.5. P/As = mole ratio in the initial solution prior to precipitation. IDL = 1.4 Fg/L			

Table 9-2. Hydroxyapatite solid solution series.

P/As mole ratio in the final solid	$\text{Ca}_w(\text{As}_x\text{P}_y\text{O}_4)_z(\text{OH})_2$				Arsenic in the final solid, %
	w	x	y	z	
0.06 ± 0.01	10	0.94	0.06	6	28.6 ± 0.7
0.6 ± 0.1	10	0.63	0.37	6	18.5 ± 2.1
1.9 ± 0.0	10	0.35	0.66	6	13.7 ± 0.4
5.7 ± 0.4	10	0.15	0.85	6	5.9 ± 0.3
8.0 ± 0.2	10	0.11	0.89	6	4.4 ± 0.2
7.9 ± 0.1	10	0.11	0.89	6	4.3 ± 0.2
12.7 ± 0.2	10	0.01	0.99	6	2.9 ± 0.1
No As	10	0.00	1.00	6	0.1 ± 0.02
Apatite	10	0.00	1.00	6	0

Table 9-3. Solid solution stoichiometry versus free energy of formation.

Compound Stoichiometry) G° , Free energy of formation	
	kcal/g-mole	kJ/g-mole
$\text{Ca}_{10}(\text{As}_{0.94}\text{P}_{0.06}\text{O}_4)_6(\text{OH})_2$	$-2,466.1 \pm 3.7$	-10318.2 ± 15.5
$\text{Ca}_{10}(\text{As}_{0.63}\text{P}_{0.37}\text{O}_4)_6(\text{OH})_2$ (non-QA)	-2671.0 ± 16.0	-11175.4 ± 66.9
$\text{Ca}_{10}(\text{As}_{0.34}\text{P}_{0.66}\text{O}_4)_6(\text{OH})_2$ (non-QA)	-2826.9 ± 1.6	-11827.7 ± 6.7
$\text{Ca}_{10}(\text{As}_{0.15}\text{P}_{0.85}\text{O}_4)_6(\text{OH})_2$	-2932.4 ± 9.3	-12269.2 ± 38.9
$\text{Ca}_{10}(\text{As}_{0.11}\text{P}_{0.89}\text{O}_4)_6(\text{OH})_2$	-2952.4 ± 4.7	-12352.8 ± 19.7
$\text{Ca}_{10}(\text{As}_{0.07}\text{P}_{0.93}\text{O}_4)_6(\text{OH})_2$	-2973.2 ± 4.2	-12439.9 ± 17.6
$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	-3014.0 ± 4.2	-12610.6 ± 17.6
$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, Literature value	-3014.3	-12611.8

Table 9-4. Arsenic in solution after aging for 6 months.

System (initial As concentration)	Arsenic in solution after aging for 6 months, Fg/L
Pure (initial As was 1,000,000 Fg/L)	3.4± 1.0
Berkeley Pit Water (initial As was 100,000 Fg/L)	7.5± 2.4
ASARCO Water (initial As was > 3,000,000 Fg/L)	28.9± 0.6
Nominal P/As mole ratio in the starting solution = 7. Precipitation was conducted at ambient temperature. Six-month aging in air-sparged vessels.	

Table 9-5. First order economic analysis.

System	FCC, \$	FCAC, \$/yr	Oper. cost, \$/yr	Total cost, \$/yr	Cost, \$/1000 gal	Cost, ¢/gal
300 gal/min., 500 ppb As	350,300	90,800	27,600	118,400	0.74± 0.21	0.07± 0.02
20 gal/min., 1 g/L As	156,800	40,700	143,700	184,300	17.5± 5.2	1.75± 0.52
For detailed calculations refer to Appendix M, Tables M1–M8.						

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